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INVESTIGATION OF CONDITIONS FOR THE ISOLATION OF CEMENTITE FROM IRON – CARBON ALLOYS

R. B. Golubtsova

A. A. Baikov Institute of Metallurgy, Academy of Sciences, USSR

(Presented by Academician I. P. Bardin, August 8, 1958)

In connection with investigations on the isotope ratio of stable carbon isotopes in natural materials, which are being carried out by the Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences USSR, the necessity has arisen for the preparation of pure cementite for the purpose of developing our methods. Work devoted to the study of the chemical properties of iron carbide has been carried out by a number of authors [1]. The isolation of iron carbide has been accomplished by chemical solution of steel in acids and by anodic solution of steel in various electrolytes. A detailed review of the work has been presented in the book by N. M. Popova [1].

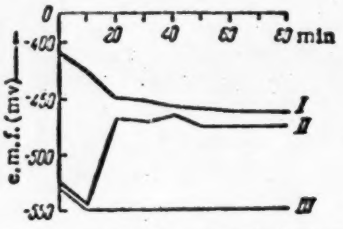

Fig. 1. Electrode potentials for Fe C alloy. Electrolytes, per 1000 ml of H_2O:
I – 5 ml HCl, 5 g of citric acid;
II – 10 ml HCl, 100 g of citric acid;
III – 75 g KCl, 5 g of citric acid.

In her investigations of carbon steel after annealing in the temperature interval 200–450°, N. M. Popova established that iron carbide has a uniform composition corresponding to the formula Fe_3C at all annealing temperatures [3]. According to the literature [1], cementite crystallizes in an orthorhombic lattice with the parameters a = 4.51 A, b = 5.079 A, and c = 6.730 A. The present work constituted a study of the conditions for the isolation of cementite from iron–carbon alloys followed by microchemical analysis of the phase. The method of the investigation was based on electrochemical, anodic solution of the metal of the sample.

In order to establish the optimum conditions for the electrolysis, the effect of the concentrations of hydrochloric and citric acids in the electrolyte, the change in the current density during the course of the experiment, and also the electrolysis time were investigated. Special experiments were carried out to establish the effect of temperature on the quantitative separation of the cementite.

The samples used in the investigation were alloys* having the chemical composition (in weight percent): C 5, Fe 95; C 2 and Fe 98%. The alloy sample being investigated served as the anode; for this purpose, it was shaped into a cylinder (length = 50 mm, diam. = 10 mm). Current density and electrolyte composition were varied. Electrolytes described in the literature for the separation of iron carbides from steel consist of a mixture of HCl (1.19), citric acid, and saturated KCl solution [4, 5].

Our investigation on the isolation of metallic compounds form complex alloys [6] showed that the separation of the carbide phase is conveniently carried out in an electrolyte consisting of a mixture of hydrochloric and citric acids without potassium chloride [6].

* The alloys were prepared by P. T. Kolomytsev.

N. M. Popova developed a method for the separation of disperse carbides of the cementite type, the method being based on anodic solution of the samples in a cooled, weakly acid solution of chlorides at low current density [7]. The author reported that in the separation of disperse cementite, a current density of not more than 0.03 amp/cm^2 must be used in order to avoid oxidation of the carbides [1].

In order to select the optimum electrolyte composition, we carried out potential measurements on alloys containing cementite; the potentials were measured against a calomel electrode [8-10]. The results of these experiments (Figure 1) show that the most favorable electrolyte was No. 1, which consisted of 5 ml of HCl (1.19), 5 g of citric acid and 1000 ml of H_2O.

During the study of the effect of the citric acid content of the electrolyte containing 5 ml of HCl (1.19) and 1000 ml of H_2O on the composition of the anode residue under conditions which included no cooling, a current density of 0.05 amp/cm^2, and an electrolysis time of 1.5 hours, it was found that an increase in the amount

TABLE 1

Effect of Current Density of the Chemical Composition of the Anode Residue. Electrolysis time, 1.5 hours (without cooling). Electrolyte Composition: 5 g of Citric Acid, 5 ml of HCl (1.19), 1000 ml of Water

Current density, amp/cm^2	Weight of powder collected, g	Found, wt. %				Found, atom %			
		Fe	C	total	Fe/C	Fe	C	total	Fe/C
0.03	0.0410	93.40	6.68	100.08	13.93	75.04	24.96	100	3.00
0.05	0.0410	93.34	6.74	100.08	13.85	74.86	25.14	100	2.97
0.07	0.0422	92.68	7.29	99.97	12.71	73.27	26.73	100	2.71
0.10	0.0520	91.42	8.61	100.03	10.61	69.54	30.46	100	2.28

of citric acid in the electrolyte had no effect on the yield of anode powder nor on the chemical composition of the powder. In all experiments, the ratio of the iron content to that of the carbon corresponded to the theoretical value or closely approximated it, which indicates the presence of cementite Fe_3C. Theoretically,

$$\frac{Fe\,(wt.\ \%)}{C\,(wt.\ \%)} = 13{,}94$$

or 3.0 atomic ratio. On the basis of these data, further experiments were carried out with an electrolyte having the composition 5 g of citric acid, 5 ml of HCl (1.19), and 1000 ml of water. From a comparison of the analytical data (Table 1), it follows that a current density of 0.03-0.05 amp/cm^2 is favorable and has no effect on the chemical composition of the Fe_3C phase.

The data from these experiments showed that the iron–carbon ratio in the phase corresponded to the stoichiometric composition of cementite.

With an increase in the current density to 0.07 amp/cm^2, partial oxidation of the carbide phase obviously occurred, as may be seen from the decrease in the Fe/C ratio from 3.0 to 2.71. At a current density of 0.1 amp/cm^2, this ratio decreased to 2.28, which indicates decomposition of the cementite residue.

In order to have a basis for determining the optimum conditions for the isolation of Fe_3C, it was necessary to confirm the reproducibility of results obtained at various electrolysis times in the same electrolyte (Table 2).

As seen from the experimental results, which exhibited good reproducibility,. in all cases and with all alloys, a compound of the stoichiometric composition Fe_3C was separated. Consequently, decomposition of the carbide phase did not occur during 1.5 hours of electrolysis. For purposes of comparison, experiments were also carried out in which the electrolyte was cooled to 0°, the temperature rising to +4° during the electrolysis. It was found (cf. Table 2) that the separation of cementite from the alloys investigated could be carried out with satisfactory results without cooling (at a current density of 0.03-0.05 amp/cm^2); this is a feature of the proposed method. Under the experimental conditions indicated, cooling of the electrolyte has no advantage.

TABLE 2

Effect of Electrolysis Time on Reproducibility of the Experimental Results. Electrolyte Composition: 5 ml HCl (1.19), 5 g of Citric Acid, 1000 ml H_2O (without cooling)

Current density, amp/cm²	Electrolysis time, min.	Weight of powder collected, g	Found, wt. %				Found, atom %			
			Fe	C	total	Fe:C	Fe	C	total	Fe:C
0.03	30	0.0136	93.44	6.72	100.16	13.90	74.94	25.06	100	2.99
0.03	60	0.0182	93.35	6.70	100.05	13.93	75.03	24.97	100	3.00
0.03	90	0.0410	93.40	6.68	100.08	13.98	75.04	28.96	100	3.00
0.05	30	0.0270	93.45	6.70	100.15	13.94	74.99	25.01	100	2.99
0.05	60	0.0270	93.35	6.70	100.05	13.93	74.94	25.06	100	2.99
0.05	90	0.0410	93.34	6.74	100.08	13.85	74.86	25.14	100	2.97

The total volume of electrolyte of the indicated composition used in the experiment was 1000 ml. The weighed sample – the anode (the ends of which were sealed with rubber tubing) – was suspended by means of a wire in the center of the anode compartment, which was formed from tracing paper. The cathode was a stainless steel, hollow cylinder. During the 1.5-hour period, the residue formed on the anode as a very dense, disperse powder. At the conclusion of an experiment, the sample was quickly submerged in a beaker containing alcohol, after which the residue was rapidly brushed off into a beaker containing water by means of a glass rod fitted with a rubber policeman. These operations must be carried out rapidly in order to avoid oxidation of the powder. The powder was centrifuged and simultaneously washed with alcohol by decantation from the test tube, and was then placed in a sealed quartz tube, and the latter was heated to 160° on an oil bath. The powder was dried in a stream of hydrogen.

The dried powder was analyzed by microchemical and x-ray • methods. For the analyses, a portion of the powder in the range of 0.01 to 0.015 g was weighed on microscales and dissolved in 10 ml of HCl (1.19), which was contained in a 100-ml beaker. After solution was complete, the solution was acidified with 4 drops of HNO_3 (1.40). The contents of the beaker were evaporated to dryness. The dry residue was moistened with 10 ml of HCl (1:1) and evaporated to a pasty consistency; the paste was cooled, 10 ml of HCl (1:1) was again added, and the transparent solution was transferred to a 100-ml volumetric flask. 2 ml of the solution was taken for the microchemical determination of iron, and was titrated with a sequestering agent, Trilon B (a disubstituted sodium salt of ethylenediaminetetraacetic acid [10, 11]), from a microburet. The carbon was determined on a microsample, which was placed in a small porcelain boat and burned in a tube furnace in a stream of oxygen at 1200°.

The results of the x-ray analysis (Figure 2) confirmed the presence of pure cementite.

Fig. 2.

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TERNARY SEMICONDUCTOR COMPOUNDS $A^I B^V B_2^{VI}$

L. D. Dudkin and A. P. Ostranitsa

A. A. Baikov Institute of Metallurgy, Academy of Sciences, USSR

(Presented by Academician I. P. Bardin, August 8, 1958)

On the basis of the features of the crystallochemical structure of semiconductors (the covalent character of the bonds, for the formation of which a specific concentration of valence electrons in the molecule is required) and on the basis of the presently available experimental material, it can be concluded that ternary semiconducting compounds are formed on the basis of binary compounds, of which one must be a semiconductor; the ratios of the molar concentrations of the initial components in the ternary compounds correspond to a ratio of simple, whole numbers.

TABLE 1

Binary components	Sb_2Se_3	Sb_2Te_3	Bi_2Se_3	Bi_2Te_3
Ag_2Se	$AgSbSe_2$		$AgBiSe_2$	
Ag_2Te		$AgSbTe_2$		$(AgBiTe_2)$
Cu_2Se	$CuSbSe_2$		$(CuBiSe_2)$	
Cu_2Te		$(CuSbTe_2)$		$(CuBiTe_2)$

The present paper is devoted to the clarification of questions relating to the existence and the physicochemical nature of hypothetical ternary compounds of the general composition $A^I B^V B_2^{VI}$ (A^I – Cu, Ag, B^V – Sb, Bi, B^{VI} – Se, Te) [1], the formation of which, by analogy to the chalcopyrite group of semiconductors $A^I A^{III} B_2^{VI}$ (A^{III} – Al, Ga, In, Tl), is assumed in the ternary systems A^I — B^V – B^{VI} along the binary sections $A_2^I B^{VI}$ – $B_2^V B_3^{VI}$ at a component ratio of 1 : 1.

In spite of the relationship between the chemical compositions of the compounds $A^I B^V B_2^{VI}$ and $A^I A^{III} B_2^{VI}$, it is easy to predict that they are nonisostructural; in order that tetrahedral sp^3 hybrid bonds may be formed, and these bonds do occur in the compounds $A^I A^{III} B_2^{VI}$, the concentration of valence electrons in the molecule (C_{el}) must be equal to or a multiple of 8 ($C_{el}^{A^I A^{III} B_2^{VI}} = 16$); in the compounds $A^I B^V B_2^{VI}$, $C_{el} = 18$.

Eight ternary alloys based on the appropriate binary compounds were prepared; the atomic compositions of these alloys are presented in Table 1.

The samples were prepared by fusing the initial components in evacuated quartz ampoules and subsequently cooling the melts in air. The alloys were investigated by methods analogous to those described previously [2].

Investigation of the microstructure of the cast samples established that only four of the eight compounds $A^I B^V B_2^{VI}$ actually exist: $CuSbSe_2$, $AgSbSe_2$, $AgSbTe_2$ and $AgBiSe_2$, and these crystallize directly from the melt. The sample having the composition $AgSbTe_2$ contained small deposits of tellurium eutectic along the grain boundaries, which were probably connected with a shift of the phase of this compound toward the antimony-rich side.

The microstructure of the alloys $CuSbTe_2$ and $CuBiTe_2$ were of the eutectic type; $CuBiSe_2$ and $AgBiTe_2$ were two-phase alloys. In Table 1, the compositions of the heterophase inclusions are enclosed in parentheses. Two week annealing of the alloys at a temperature of 350° did not appreciably change their microstructures.

The crystallization temperatures of the ternary compounds (Table 2) were determined from the heating and cooling curves of the single-phase alloys, and these same curves also confirmed that the compounds melted

TABLE 2

Compound	Transformation temp., °C	ΔE, eV	σ, ohm^{-1} cm^{-1}	α, μv/degree	$K_{ct} \cdot 10^3$, cal/degree·cm·sec	H_m, kg/mm^2
$AgSbSe_2$	m.p. 634	0,58	0,78	+418	2,5	208
$AgSbTe_2$	m.p. 561	—	306 120	+129 +228	2,1	75
$AgBiSe_2$	m.p. 792 α⇄β 298	α—0,34 β—1,10	23[1] 42[2]	—106[1] —144[2]	2,45	194
$CuSbSe_2$	m.p. 472	0,16 0,80	4,0[3] 0,39[4]	+394[3] +343[4]	3,4	199

[1]Quenched from 600°. [2]Annealed at 150°. [3]Quenched from 400°. [4]Annealed at 150°.

congruently. A thermal effect at a temperature of 298° was observed with the compound $AgBiSe_2$. A comparison of the x-ray patterns of alloys quenched from temperatures above and below this effect showed that the effect is connected with a polymorphic transformation of the ternary compound.

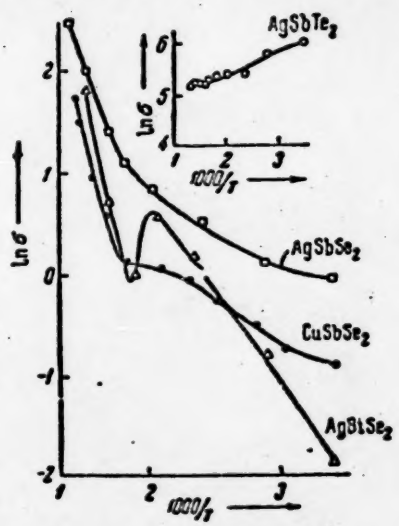

Fig. 1. Temperature dependence of the electrical conductivity of the ternary alloys.

The specific electrical conductivity (σ), the thermal electromotive force (α), and the microhardness (Hm) (Table 2) were determined for the equilibrium alloys corresponding to the compounds $AgSbSe_2$, $AgSbTe_2$, $CuSbSe_2$, and $AgBiSe_2$. On the basis of the measured values of the overall thermal conductivity and the values of the electronic thermal conductivity, the coefficients of lattice thermal conductivity were evaluated for the ternary alloys (Table 2) by means of the Wiedemann-Franz rule.

The results of the measurements of the temperature dependence of the electrical conductivity of the compounds $A^IB^VB_2^{VI}$ are presented in Figure 1. The alloys of the composition $CuSbSe_2$, $AgSbSe_2$, and $AgBiSe_2$ exhibited dependences σ(T) of the type characteristic of semiconductors. In the case of the latter compound, the curve of lnσ(1/T) had a sharp inflection at a temperature close to that of its polymorphic transformation.

The energy of activation of the current carriers in the ternary compounds were calculated from σ(T) (Table 2).

The course of the temperature dependence of the electrical conductivity of the alloy $AgSbTe_2$ up to 500° was like that of a metal, which may be explained by the results of the investigation of its microstructure. However, the absolute values of the thermoelectric properties of $AgSbTe_2$ indicate that the phase corresponding to this compound is semiconducting in nature.

Analysis of the powder patterns of the ternary alloys showed that the compounds $AgSbSe_2$ and $AgSbTe_2$ have face-centered lattices with constants (a) of 5.77 and 6.07A, respectively. During the period in which our investigations were carried out, a paper [3] appeared which confirmed these results. Moreover, this paper also gave the positions of the atoms in the unit cell: Ag and Sb 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\,0\,\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\,0$, Se and Te $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\,00$, $0\,\frac{1}{2}\,0$, $00\,\frac{1}{2}$. The compound $CuSbSe_2$ and the α-modification of the compound $AgBiSe_2$ have more complex structures.

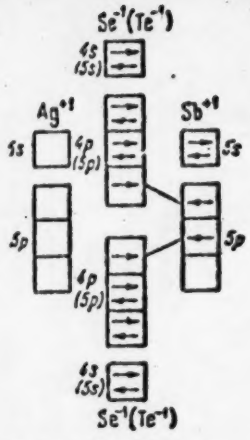

Fig. 2. Scheme of the chemical bonding in the compounds $AgSbSe_2$ and $AgSbTe_2$.

The determination of the structure of β-$AgBiSe_2$ requires a high-temperature x-ray pattern; on the patterns of samples quenched from 600°, there were several weak interference lines corresponding to lines of the α-modification; these lines were in addition to intense lines corresponding to a face-centered lattice.

The corresponding binary components of thecompounds of the type $A^IB^VB_2^{VI}$ have a related crystallochemical nature. Therefore, the reasons for the stability of the ternary compounds must be sought in the peculiarities of their chemical structure.

In order to clarify the nature of the interatomic bonds leading to the formation of semiconductors of the type $A^IB^VB_2^{VI}$, we started with an analysis of the crystal structure of $AgSbSe_2$ and $AgSbTe_2$, the basic features of which are the equality of the interatomic distances Ag–Se (Te) and Sb–Se (Te), the right angle between the bonds, the qualitative identity of the position in the lattice of the atoms of Group VI [$Se_I(Te_I)$coordinates 4 Sb and 2 Ag, $Se_{II}(Te_{II})$–2 Sb and 4 Ag], and the increase in the coordination number of the antimony atoms [6] over their maximum valence. The latter fact, according to L. Pauling [4], indicated the presence of one unfilled band in the antimony atoms in crystals of the ternary compounds.

Figure 2 presents a scheme of the states of the bonding electrons of the atoms in $AgSbSe_2$ and $AgSbTe_2$; this scheme takes into account the features mentioned above.

On the basis of values of the ionic and covalent radii [5] and on the basis of the assumption that, for a given atomic species, the filling of the bands with electrons is accompanied by a change of the same amount in the dimensions of the atoms, we found the following radii: Sb^+, Se^- and Te^-: 1.30, 1.58 and 1.79 A, respectively. Considering the approximate nature of our calculations, it appears that the calculated values of the interatomic distances ($Ag^+ - Se^- = 2.84$ A, $Sb^+ - Se^- = 2.88$ A. $Ag^+ - Te^- = 3.05$ A, $Sb^+ - Te^- = 3.03$ A) are in a good agreement with the actual interatomic distances in the compounds $AgSbSe_2$ and $AgSbTe_2$ (2.88 and 3.04 A).

Assuming that the scheme presented in Figure 2 is the most characteristic one for all of the compounds $A^IB^VBE^{VI}$, it is possible to deduce the basic qualitative conditions determining their stability.

Since, according to the scheme of Figure 2, covalent bonds are formed between the atoms B^V and B^{VI}, they are the "rigid" basis of the crystal lattice. The ions A^I are disposed inside this framework in conformity with the requirement for neutralization of the negative charges. Therefore, in the case where the atoms A^I and B^V have considerably different volumes, a loose, unstable lattice must be formed. The effect of this chiefly geometric factor can explain the instability of the compounds $CuBiSe_2$ and $CuBiTe_2$, in which there is more than a 60% difference in the ionic radii of Cu^+ and Bi^+.

A second stabilizing condition is the rather large difference between the electronegativity of the elements of Group VI and that of the electropositive atoms A^I and B^V. The change in this factor can explain the existence of the compounds $CuSbSe_2$ and $AgBiSe_2$ and the instability of the analogous compounds with tellurium.

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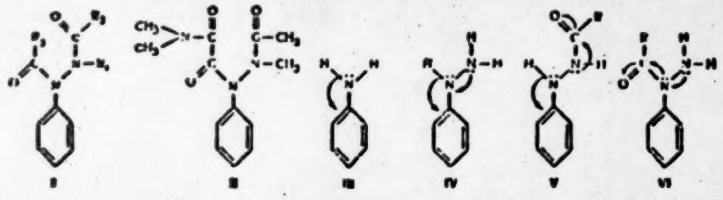
THE CHEMICAL STRUCTURE AND CERTAIN PROPERTIES OF DIACYL DERIVATIVES OF PHENYLHYDRAZINE

N. I. Latosh and Z. V. Pushkareva

S. M. Kirov Ural Polytechnical Institute

(Presented by Academician L. N. Nazarov, November 20, 1956)

In a previous communication [1], we described the preparation of diacylphenylhydrazines of the general formula (I), which are analogs of the analgestic dioxypyramidon (II) but which are less toxic than pyramidon and yet have quite as good an analgesic action.



In addition to pharmacological tests, the absorption spectra in the ultraviolet region and the dipole moments of these substances were also studied. Consideration of the ultraviolet spectra of the mono- and diacylhydrazines, both substituted and unsubstituted at the β-nitrogen atom (R_1) permitted us to trace the effect of various R_1, R_2, and R_3 radicals on the electronic structure of the molecules as a whole.

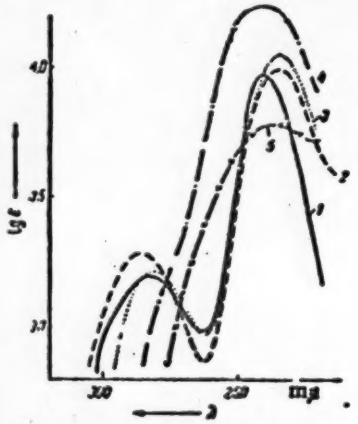


Fig. 1. 1) Phenylhydrazine; 2) aniline; 3) β-acetylphenylhydrazine; 4) acetanilide; 5) α-acetylphenylhydrazine.

Spectra were obtained for 30 substances; 22 of the spectra were taken for the first time*. The spectra were recorded with an SF-4 spectrophotometer; the substances were dissolved in absolute alcohol at a concentration of 10^{-3} mole/liter. The results are presented in the form of curves showing the change in the absorption coefficient (ε) with wavelength, and are also presented in Table 1. A comparative consideration of the spectra permitted the following, not uninteresting observations.

It is seen from Figure 1 that the spectrum of unsubstituted phenylhydrazine (Curve 1) does not differ in form from that of aniline (Curve 2), but the second maximum for phenylhydrazine is shifted 6 mμ in the long wavelength direction. The introduction of an acetyl group at the β-nitrogen atom has very little effect on the optical properties of the molecule (Curve 3); on the

* The spectra of the individual monoacyl derivatives and the anilides have been obtained previously [2]; however, they were again obtained in the present work in order to assure reliable comparisons.

TABLE 1

Prep. No.	Substance	M.p., °C	Ultraviolet Spectra				$\mu_{exp} \cdot 10^{18}$
			maxima		minima		
			λ, mμ	lg ε	λ, mμ	lg ε	
1	Aniline		286	3.240	262	2.870	1.53 [4]
			235	3 990			
2	Phenylhydrazine	20	283	3.200	263	2.980	1.7 [3]
			241	3.970			
3	β-Acetylphenylhydrazine	129	281	3.220	252	2.870	4.61
			234	4.055			
4	β-Benzoylphenylhydrazine	168	274	3.550	260	3.460	
			235	4.210			
5	β-Acetyl-β-methylphenylhydrazine	94	282	3.195	259	2.544	
			234	4.086			
6	α-Acetylphenylhydrazine	125	238	3.780			2.74
7	α,β-Diacetylphenylhydrazine	107	228	3.861			
8	α,β-Diacetyl-β-methylphenylhydrazine	b.p. 175–8/5 mm	228	4.012			3.75
9	α-Diethylaminoacetyl-β-methyl-β-acetylphenylhydrazine	b.p. 160–1°/5 mm	263	4.014			3.82
10	α-Phenylacetyl-β-methyl-β-acetylphenylhydrazine	82	228	3.900			4.08
11	α-Cinnamoyl-β-methyl-β-acetylphenylhydrazine	143	293	4.284	245	3.302	4.34
			222	4.215			
12	α-Benzoyl-β-methyl-β-acetylphenylhydrazine	114	258	3.568	274	3.556	5.56
			215	3.950			
13	α-(p-Bromobenzoyl)-β-methyl-β-acetylphenylhydrazine	126	263	3.970			4.72
			229	4.274			
14	α-(o-Hydroxybenzoyl)-β-methyl-β-acetylphenylhydrazine	180	not clearly expressed, absorption region from 308 mμ				6.52
15	α-(p-Dimethylaminobenzoyl)-β-methyl-β-acetylphenylhydrazine	154	325	4.438	276 5	3.715	7.33
			230	4.173			
16	α-Isonicotinyl-β-methyl-β-acetylphenylhydrazine	165	263	3.847	245	3.269	4.24
			215	4.150			
17	α,β-Dibenzoyl-β-methylphenylhydrazine	145	222	4.239			5.85
18	N,N'-Diacetylhydrazobenzene	105	222.5	4.082			4.51
19	N,N'-Dibenzoylhydrazobenzene	161	257	4.150			4.53
			221	4.451			
20	N-Benzoyl-N'-acetylhydrazobenzene	149	not clearly expressed				4.85
21	Dioxypyramidon	105	240	3.971			4.42
22	Pyramidon	127	269	3.987	255	3.943	
			237	4.039			
23	Acetanilide	114	240	4.240			3.72
24	Diethylaminoacetanilide	b.p. 154–5°/1 mm	242	4.230			3.98
25	Phenylacetanilide	117	244	4.260			3.36
26	Cinnamanilide	151	295	4.412	240	3.605	3.83
			221	4.265			
27	Benzanilide	163	267	4.200	241	4.021	3.38 [5]
			222	4.194			

TABLE 1 (continued)

Prep. No.	Substance	M.p., °C	Ultraviolet Spectra				$\mu_{exp} 10^{18}$
			maxima		minima		
			λ, mμ	lg ε	λ, mμ	lg ε	
28	p-Bromobenzanilide	201	269	4.186	254	4.150	
			241	4.184			
29	Salicylanilide	135	271	4.247	238	3.976	4.09
30	Isonicotinanilide	172	273	4.031	240	3.592	

other hand, the introduction of an acetyl at the α-nitrogen atom leads to a sharp change in the spectrum (Curve 5) as compared to the spectrum of unsubstituted phenylhydrazine. The absorption maximum for α-acetylphenylhydrazine lies in the same region as the maximum for acetanilide (Curve 4), and differs from it merely in intensity.

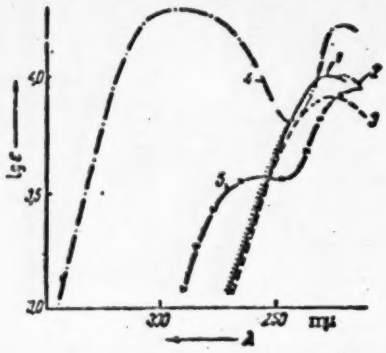


Fig 2. 1) α,β-diacetyl-β-methylphenylhydrazine; 2) α-diethylaminoacetyl-β-acetyl-β-methylphenylhydrazine; 3) α-phenylacetyl-β-acetyl-β-methylphenylhydrazine; 4) α-cinnamoyl-β-acetyl-β-methylphenylhydrazine; 5) α-benzoyl-β-acetyl-β-methylphenylhydrazine.

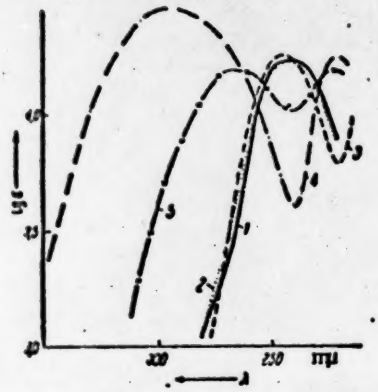


Fig. 3 1) Acetanilide; 2) diethylaminoacetanilide; 3) phenylacetanilide;; 4) cinnamanilide; 5) benzanilide.

In the case of aniline, phenylhydrazine, and β-acetylphenylhydrazine, the unshared pair of electrons of the α-nitrogen atom are apparently conjugated with the π-electrons of the benzene ring (Formulas III, IV, and V), but with the introduction of an acetyl or other acyl group into the α-position, the unshared pair of electrons of the α-nitrogen atom are attracted toward the carbonyl group, and conjugation is disturbed (Formula VI).

In the case of α,β-diacylhydrazines, the character of the ultraviolet spectra depends to a great extent on the chemical structure of the R_3 radical in the α-acyl group (Figure 2). Moreover, the introduction of polar groups into the α-acyl group, but not bonded to the carbonyl "conductors" of the conjugation (double bonds, phenyl groups, etc.), causes almost no change in the absorption spectra as compared to the unsubstituted α-acetyl derivative (Curves 1, 2, and 3). The presence in the α-acyl group of substituents bonded to the carbonyl "conductor" of conjugation leads to a radical change in the absorption spectra. This may be seen from the curves for the α-cinnamoyl and α-benzoyl derivatives (Curves 4 and 5).

The nature of the effect of a radical attached to the α-acyl group of a diacylphenylhydrazine on the electron system of the molecule can be seen not only in the spectra of the diacylhydrazines, but also in the spectra

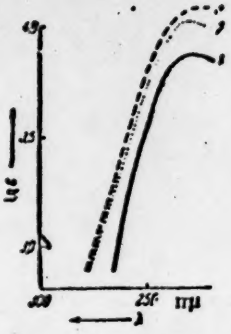


Fig. 4. 1) α,β-Diacetylphenylhydrazine; 2) α,β-diacetyl-β-methylphenylhydrazine; 3) N,N'-diacetylhydrazobenzene.

of the simpler "model" molecules—anilides of the acids corresponding to the α-acyl group (Figure 3). Precisely the same regularity is observed here as in the case of the diacyl derivatives of phenylhydrazine (Figure 2).

In other words, the spectra of the various diacyl derivatives of phenylhydrazine differ from one another in the same manner as the spectra of the anilides of the acids corresponding to the α-acyl group. Moreover, the similarity of the spectrum of the anilide to the spectrum of the corresponding diacylphenylhydrazine is closest in those cases where there is a considerable conjugation effect in the α-acyl group.

In the case of the α-benzoyl derivatives of β-acetyl-β-methylphenylhydrazines and also in the case of the corresponding anilides, the introduction of electron-donor substituents into the o- or p-position of the benzene ring (R_3) exerts a stronger effect on the change in the spectrum (as compared to the unsubstituted α-benzoyl derivative) than does the introduction of electron-acceptor substituents.

A comparison of the spectra presented in Figure 4 is interesting. It appears that the introduction at the β-nitrogen atom of methyl or phenyl radicals or of an acyl group has a slight effect on the optical properties of the molecule.

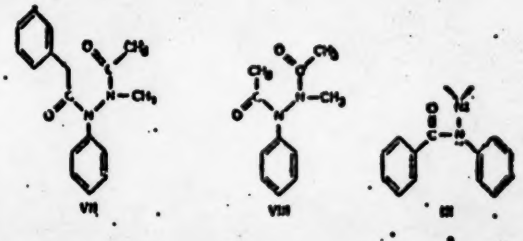
Since the aim of the present work was to shed some light on questions relating to the connection between chemical structure and analgesic activity of phenylhydrazine derivatives and since their polar properties are very significant with respect to this connection, we also measured the dipole moments of 21 of the compounds synthesized (of which, 20 were measured for the first time). The measurements of the dipole moment and density of solutions of the compounds were carried out by the beat method in benzene at 25° ± 0.01°.

Attention is directed to the similarity in the experimental values of the dipole moments of anilides of acids in which the structures of the acid radicals are very different (Nos. 23-29 in Table 1); moreover, these values differ little from the dipole moments of acetamide [6] ($\mu = 3.72$ D) and benzamide [6] ($\mu = 3.60$ D). It is apparent that these values of the dipole moments of anilides and amides are predominantly determined by the distribution of electron density in the amide part of the molecule.

The dipole moment of phenylhydrazine ($\mu = 1.7$ D) differs little from the dipole moments of anilide ($\mu = 1.53$ D) and hydrazine ($\mu = 1.83$ D); i.e., the moments of N—H, N—C_6H_5 and N—NH are approximately compensating. Apparently, the angles between the bonds H—N—H, H—N—C_6H_5, and H—N—N are approximately the same and equal to that in hydrazine [7].

The dipole moments of diacylhydrazines differing in the structure of the α-acyl group differ little from the dipole moments of the corresponding anilides in those cases where the acyl group is a substituted or unsubstituted acetyl (Nos. 8, 9, 10, and 11, and 23, 24, 25, and 26, in Table 1) and differ sharply when the acyl group is a substituted or unsubstituted benzoyl (Nos. 12, 13, 14 and 15, and 27, and 29 in Table 1).

It is not clear, at first glance, why there is a sharp increase in the dipole moment of α-benzoyl-β-acetyl-β-methylphenylhydrazine as compared to VIII if cognizance is taken of the fact that the dipole moments of acetanilide and benzanilide are approximately the same (3.72 and 3.32 D) and that the right hand part of the molecules are identical.



The hypothesis arises that the considerable electron-conjugation effect in the benzoic acid hydrazide system (IX) leads to the formation of a planar molecule. This is confirmed by a calculation carried out by vector summation (for (VIII), μ_{calc} for a planar structure is 5.02 D).

In conclusion, it should be pointed out that not one of the compounds investigated has either free rotation about the N–N hydrazine bond or a trans configuration of the acyl group.

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HIGH-TEMPERATURE CONDENSATION OF ALKYLDICHLOROSILANES WITH CHLOROOLEFINS

V. F. Mironov, Corresponding Member AN SSSR A. D. Petrov and V. V. Pisarenko

N. D. Zelinksii Institute of Organic Chemistry, Academy of Sciences, USSR

Agre [1, 2] has recently shown that when a mixture of polychloroethylenes and trichlorosilane is passed through a tube heated to 500-600°, condensation occurs accompanied by elimination of HCl, and polychlorovinyltrichlorosilanes are formed:

$$Cl_2C{=}CHCl + HSiCl_3 \xrightarrow{600^\circ} Cl_2C{=}CHSiCl_3 + HCl,$$

$$ClCH{=}CHCl + HSiCl_3 \xrightarrow{600^\circ} ClCH{=}CHSiCl_3 + HCl.$$

We have shown [3, 4] that trichlorosilane can be replaced in these reactions by CH_3HSiCl_2 and $C_2H_5Cl_2SiH$, thus making possible the synthesis, in good yields, of dichlorosilanes formed during the hydrolysis of linear siloxane polymers.

Finally, we discovered [4] that yields of more than 50% of vinylmethyldichlorosilane can be obtained by condensation of vinyl chloride and CH_3Cl_2SiH in an empty glass tube at high temperature (600°).

$$CH_2{=}CHCl + HSiCl_2CH_3 \xrightarrow{600^\circ} CH_2{=}CHSiCl_2CH_3.$$

In the present investigation, we found* that $C_2H_5SiCl_2H$ condenses with vinyl chloride to give a good yield of vinylethyldichlorosilane; the yield (27%) is not changed if the glass tube is packed with glass rods. A change from an empty glass tube to an iron tube also has substantially no effect on the yields of $RCl_2SiCH{=}CH_2$. However, trialkylsilanes cannot be condensed with vinyl chloride, and in this case the reaction proceeds differently:

$$(C_2H_5)_2CH_3SiH + ClCH{=}CH_2 \xrightarrow{600^\circ} (C_2H_5)_2CH_3SiCl + CH_2{=}CH_2.$$

We further found that the condensation of CH_3Cl_2SiH with both cis- and trans-dichloroethylenes leads to the same results, to a 20% yield of $ClHC{=}CHSiCl_2CH_3$ and an 18% yield of $Cl_2CH_3SiCH{=}CHSiCH_3Cl_2$, the structure of which was proved by methylation and by the complete correspondence of the Raman spectrum** with known $(CH_3)_3SiCH{=}CHSi(CH_3)_3$ [6].

It is interesting to note that regardless of whether methallyl chloride or 2-methylpropenyl chloride is used in the condensation, in either case was obtained chiefly $Cl_2(CH_3)SiCH{=}C(CH_3)_2$ (~13%), insignificant amounts of $Cl_2(CH_3)SiCH_2(CH_3)C{=}CH_2$, and a mixture of xylenes.

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* The Wegenberg patent [5] relating to this reaction became known to us after completion of the previous [4] and the present work

** In the present work, the Raman (RS) and infrared (IR) spectra were obtained and interpreted by L. A. Leites and Yu. P. Egorov, to whom we express our sincere appreciation.

Allyl chloride also condenses with methyldichlorosilane to give a 30% yield of allylmethyldichlorosilane and some propenylmethyldichlorosilane; however, when this reaction is carried out in an iron tube, considerable amounts of propenylmethyldichlorosilane are formed. Aryl chlorides also undergo this high temperature condensation in a manner similar to chloroolefins. Thus, for example the following reaction occurs with a 13% yield:

$$C_2H_3C_6H_4Cl + Cl_2Cl_2SiH \xrightarrow{600^\circ} HCl + CH_3Cl_2SiC_6H_4C_2H_3.$$

Saturated alkyl halides, methyl, propyl, and isopropyl chlorides and dichloromethane, proved to be incapable of undergoing condensation with silanes containing and Si–H bond. The condensation of CH_3Cl_2SiH with ethylene proceeds by an unexpected, but interesting route; vinylmethyldichlorosilane is obtained in 14% yield as the major product of the reaction:

$$CH_3Cl_2SiH + CH_2 = CH_2 \rightarrow CH_3Cl_2SiCH = CH_2 + H_2.$$

Finally, we attempted to carry out the condensation of $ClCF = CF_2$ with CH_3Cl_2SiH. However, at temperatures above 500°, flame and sharp reports continuously occurred in the reaction tube, sometimes leading to destruction of the tube. Nevertheless, from the resulting condensate we were able to isolate a fraction boiling at 97-100°, $n^{20}D$ 1.3904, d^{20}_4 1.3311, which probably (on the basis of the Raman spectrum) contained $CH_3Cl_2SiF = CF_2$.

EXPERIMENTAL

Vinylethyldichlorosilane $CH_2 = CHSiCl_2C_2H_5$. A stream of vinyl chloride was passed (at 15 liters/hour) through an empty glass tube, 20 mm in diameter and 600 mm long, heated to 560°. To this same tube was added 300 g of $C_2H_5Cl_2SiH$ at a rate of 1 drop per second, the addition requiring 3 hours and 40 minutes. 246 g of condensate was collected in a trap cooled with ice, and distillation of the condensate in a column gave 60 g of vinylethyldichlorosilane, b.p. 122.5°(753 mm) $n^{20}D = 1.4398$; $d^{20}_4 = 1.0712$; MR_D obtained 38.15, calculated 38.21. The yield was 16.7% or 25% of the reacted $C_2H_4Cl_2SiH$. Literature data [7, 8]: b.p. 127-128°; $n^{20}D$ 1.4302, d^{20}_4 1.0461, b.p. 119°/748 mm, $n^{20}D$ 1.4385, d^{20}_4 1.0664.

β-Chlorovinylmethyldichlorosilane $ClCH = CHSiCl_2CH_3$. 1,2-bis(Methyldichlorosilyl)ethylene $CH_3Cl_2SiCH = CHSiCl_2CH_3$. A mixture consisting of 190 g of methyldichlorosilane and 150 g of trans-dichloroethylene was passed through the above described tube at 600° for 3.5 hours. Distillation of the condensate in a column gave 48 g of β-chlorovinylmethyldichlorosilane [4], b.p. 138-139°, $n^{20}D$ 1.4690; d^{20}_4 1.2629; and 42 g of $CH_3Cl_2SiCH = CHSiCl_2CH_3$, b.p. 196°, $n^{20}D$ 1.4870.

Raman spectrum: 165 (5); 206 (2); 242 (0); 300 (3); 335 (2b); 432 (1b), 486 (10); 496 (7); 548 (2 v.b.); 702 (1 s.l.); 718 (0); 796 (0); 996 (2 s); 1030 (1 p); 1260 (0); 1289 (10s); 1400 (3); 1572 (2 s.l.); 1613 (0); 2871 (0); 2907 (10); 2950 (3); 2975 (7);

Infrared spectrum: 753 (w); 766 (w); 848 (w); 918 (w); 947 (w); 1005 (s); 1036 (w); 1076 (w); 1123 (av); 1180 (s); 1262 (s); 1318 (w); 1341 (w); 1362 (w); 1405 (s); 1561 (v.w.); 1614 (v.w.);

A similar experiment with cis-dichloroethylene led to practically the same result.

2-Methylpropenylmethyldichlorosilane $CH_3Cl_2SiCH = C(CH_3)_2$ A. A mixture consisting of 130 g of 2-methylpropenyl chloride [9] and 157 g of methyldichlorosilane was passed through a tube at 600°. Two-fold distillation in a column gave 22 g of a fraction boiling at 138-141° and 29 g of 2-methylpropenylmethyldichlorosilane; b.p. 153°; $n^{20}D$ 1.4582; d^{20}_4 1.0697; MR_D found 43.41, calculated 43.41. The yield was 15%.

Found %: C 35.90; 35.78; H 6.19; 6.13; Cl 42.93; 42.56; Si 16.13; 15.81 $C_5H_{10}SiCl_2$. Calculated %: C 35.50; H 5.95; Cl 41.92; Si 16.60

Raman spectrum: 173 (2b); 219 (5); 245 (2); 266 (0); 303 (2b); 370 (5); 438 (5); 450 (4); 470 (1); 510 (5b); 542 (1b); 710 (4); 754 (1b); 797 (0); 858 (1); 968 (0); 1068 (3); 1147 (2b db.) 1181 (0); 1216 (1b); 1259 (0); 1310 (3); 1336 (0b); 1380 (6); 1410 (1); 1447 (8); 1623 (10); 2858 (2b); 2915 (10); 2944 (3p); 2983 (8b).

Methylation of $CH_3Cl_2SiCH = C(CH_3)_2$ led to $(CH_3)_3SiCH = C(CH_3)_2$, which was identical to a previously prepared sample [10] in constants and Raman spectrum.

The fraction boiling at 138-141° was also methylated with CH_3MgCl; distillation of the reaction products gave two fractions: 109-111° (I) and 138-140° (II). Raman spectra were obtained for these two fractions, and it was found that Fraction I was mainly $(CH_3)_3SiCH_2C(CH_3)=CH_2$, the spectrum of which was obtained previously [10], while Fraction II consisted of paraxylene and metaxylene with some $(CH_3)_3SiCH_2C(CH_3)=CH_2$.

B. A mixture consisting of 320 g of methyldichlorosilane and 205 g of methallyl chloride was passed for 5 hours through a tube heated to 600°. Distillation of the condensate in a column gave 52 g of a fraction boiling at 138-141°, the spectrum of which was identical with the spectrum of this same fraction obtained in Experiment A, and 34 g of 2-methylpropenylmethyldichlorosilane, the spectrum of which was in complete agreement with the spectrum of $CH_3Cl_2SiCH=C(CH_3)_2$ from Experiment A.

Allylmethyldichlorosilane $CH_2=CHCH_2SiCl_2CH_3$. A mixture consisting of 400 g of methyldichlorosilane and 220 g of allyl chloride was passed for 6 hours through a tube heated to 600°. Two-fold distillation of the condensate in a column gave two fractions: 106-108° (I), 38 g, and 88 g of methylallyldichlorosilane (II, b.p.120°/746 mm); $n^{20}D$ 1.4419; d^{20}_4 1.0743; MR_D found 38.23, calculated 38.51. The yield was 32.6%.

Raman spectrum: 197 (0); 228 (3b); 299 (1b); 328 (0); 393 (1); 410 (2); 469 (8b); 545 (1b); 602 (1b); 649 (0); 710 (2b); 773 (0b); 807 (1b); 914 (1b); 1107 (0b); 1172 (3b); 1300 (4); 1318 (1); 1390 (2); 1422 (2); 1636 (10); 2912 (7); 2978 (2); 3011 (2); 3077 (2).

The spectrum of Fraction I (b.p. 106-108°) showed that it contained $CH_3Cl_2SiCH_2CH=CH_2$ and much benzene and other aromatic hydrocarbons.

Vinylmethyldichlorosilane $CH_2=CHSiCl_2CH_3$. A stream of ethylene (15 liters/hour) and 180 g of CH_3Cl_2SiH were passed for 2 hours through an empty iron tube heated to 600°. Distillation of the reaction products in a column gave 20 g of a substance boiling at 89-93° which contained (on the basis of Raman spectra) mainly vinylmethyldichlorosilane and some ethylmethyldichlorosilane.

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POLYCONDENSATION OF THE ETHYL ESTER OF GLYCINE IN THE PRESENCE OF ITS CARBAMATE

K. T. Poroshin, Yu. I. Khurgin and T. D. Kozarenko

N. D. Zelinksii Institute of Organic Chemistry, Academy of Sciences, USSR

(Presented by Academician B. A. Kazanskii, August 29, 1958)

The first stage in the polycondensation of α-amino acid esters in the presence of carbon dioxide is the formation of the carbamate [1].

$$R'OOC \cdot CHR \cdot NH_3^+ \cdot {}^-OOC \cdot NH \cdot CHR \cdot COOR'.$$

This reaction proceeds practically instantaneously in comparison with all of the subsequent reactions [2]. It can be assumed that the course of the polycondensation and the kinetics of the change in composition of the reaction products is determined by the amount of carbamate with respect to the amount of amino acid ester (the monomer). It was previously shown that under otherwise equivalent conditions, the course of the polycondensation is determined by the initial relative concentration of the initiator [3] and consequently, of the carbamate. In the absence of substances which act as initiators, both amino acid esters and their carbamates are relatively stable compounds. However, in a mixture of the two, for example, after the addition of carbon dioxide to an excess of amino acid ester, they interact, i.e. polycondensation takes place. Hence it follows that the actual initiator of polycondensation of α-amino acid esters is the carbamate, and not carbon dioxide, which serves as a source of carbamate by interaction with the ester. Consequently, when carbon dioxide is added to an amino acid ester, the stage in which the carbamate is formed is not required for polycondensation; i.e. polycondensation can occur if the carbamate is added directly to the monomer. On this basis, it would be expected that the rate of polycondensation and the product composition cannot depend on the method used to introduce the initiator (whether by adding a given amount of carbon dioxide or by the direct addition of the corresponding amount of carbamate).

The formation of carbamates is a typical reaction of aliphatic amines with carbon dioxide [4]; among the amine compounds undergoing this reaction are the amino acidderivatives with a blocked carboxyl group (amino acid esters and amides [2, 5, 6]):

$$2R_1R_2NH + CO_2 \rightleftarrows R_1R_2NH_2^+ {}^-OOCNR_1R_2.$$

The equilibrium is shifted completely to the right under the usual conditions [2, 6]. Therefore, under the conditions under which we previously carried out the polycondensation, all of the added carbon dioxide was bound by the amino acid ester. Carbamates of amino acid esters are comparatively stable at room temperature. Thermal decomposition of the carbamate of the ethyl ester of glycine begins at a temperature above 55°.

The aim of the present work was to confirm the initiating function of carbamates during polycondensation of α-amino acid esters in the presence of carbon dioxide. The results of measurements of the rate of monomer consumption during the polycondensation of the ethyl ester of glycine are presented below for the case in which the reaction was initiated by the addition of the corresponding carbamate.

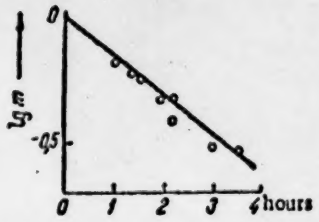

Fig. 1. Kinetics of the consumption of monomer during the polycondensation of the ethyl ester of glycine in the presence of its carbamate (1/m = 0.05; 40°).

The ethyl ester of glycine – both that used as the monomer and that used for the preparation of the carbamate – was distilled and used immediately after the distillation. The carbamate was formed in the reaction flask by placing in the flask the required number of drops of ester (the amount was accurately determined by weighing), adding absolute ester, and slowly bubbling dry carbon dioxide through the solution at −40°. After evaporation of the solvent, the completeness with which the carbamate was formed was determined from the weight increase, which was due to the carbon dioxide which had reacted with the ester. The prescribed number of drops of monomer, the amount of which was again determined accurately by weighing, were distilled into the flask, which was precooled to −40°. It was found that the desired relative initial concentration of carbamate could be obtained with an accuracy of ± 1% by counting the number of drops. All experiments were carried out at −40° and an initial relative concentration of initiator, 1/m, of 0.05. Consequently, the amount of glycine ester used for the preparation of the carbamate was one-tenth that used as monomer. The amount of free monomer was determined gravimetrically after extraction of the hydrochloride with absolute ether [7]. The data on monomer consumption are presented in Figure 1, from which it is seen that this is a first order reaction; i.e., the order of the reaction is the same as when the initiator is carbon dioxide. The rate constant for the consumption of monomer k_3 was $7.72 \cdot 10^{-5}$ $sec^{-1} \cdot mole^{-1}$. We have previously shown that the rate of monomer consumption increases with an increase in initiator concentration [3]. For the initial relative concentrations of carbamate used previously [3], down to 1/m = 0.05, the average value of $k_0 = k/(1/m)$ was $1.73 \cdot 10^{-3}$ $sec^{-1} \cdot mole^{-1}$ for initiation by carbon dioxide. In the present work in which carbamate was used as the initiator, k_0 was $1.55 \cdot 10^{-3}$ $sec^{-1} \cdot mole^{-1}$, i.e., k_0 is practically independent of the method of introduction of carbamate. As seen from Figure 1, the first, rapid stage of monomer consumption is absent when the reaction is initiated with carbamate. On the other hand, when the reaction is initiated with carbon dioxide, there is observed at the beginning of the reaction a fast stage, since on extrapolation, the kinetic curves, which are linear when plotted on semilogarithmic coordinates, intersect the ordinate axis at points which correspond to a lower initial monomer content than was used in the experiment.

A study of the polycondensation products by paper chromatography showed that the qualitative composition of the product does not depend on the method used to form the initial reaction mixture.

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INVESTIGATION IN THE FIELD OF DIACETYLENE DERIVATIVES

INTERACTION OF DIACETYLENE WITH PHENOLS, THIOPHENOL, AND BENZYL ALCOHOL

M. F. Shostakovskii, A. V. Bogdanova and G. I. Plotnikova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

(Presented by Academician B. A. Kazanskii, May 17, 1958)

We have previously reported on syntheses based on the reaction of diacetylene with aliphatic and hydroaromatic alcohols and with ethyl mercaptan [1, 2]. These syntheses made it possible to prepare ethynylvinyl ethers and sulfides of the general formula $CH_3{-}C{\equiv}C{-}CH{=}CH{-}OR(SR)$, acetals of butynal $CH_3{-}C{\equiv}C{-}CH(OR)_2$ and di[alkylthio-(arylthio)] -1,3-butadienes $RS{-}CH{=}CH{-}CH{=}CH{-}SR'$.

TABLE 1

Expt. No.	Mole ratio diacetylene: thiophenol	Amout KOH, % of thiophenol	Maximum reaction temperature, °C	Yield, % of theoretical	
				sulfide (II)	dithiophenyl-1,3-butadiene (V)
1	2:1	2	35-40	63.1	–
2	1:1	2	35-40	44.6	–
3	1:1	0.5	25-30	31.4	17.7
4	1:2	0.2	35-40	–	68.1

Since we desired to add the corresponding aryl derivatives to the list of available substances, we attempted to add phenol to diacetylene. However, under the conditions used for alcohols, phenol did not react with diacetylene in the usual manner. Assuming that the reason for this was the effect of the benzene ring transmitted through the oxygen atom, we decided to study the interaction of diacetylene with thiophenol and with benzyl alcohol on the assumption that this effect would be changed by the sulfur atom in thiophenol and by the distance of the benzene ring from the oxygen atom in benzyl alcohol. Indeed, investigation of this reaction showed that benzyl alcohol and thiophenol smoothly react with diacetylene under mild conditions according to:

$$CH{\equiv}C{-}C{\equiv}CH \xrightarrow{RXH} CH{\equiv}C{-}CH{=}CH{-}XR, \qquad (1)$$

where $RX = C_6H_5CH_2{-}O{-}$ (I); $C_6H_5{-}S{-}$ (II).

The addition of a second molecule of benzyl alcohol or thiophenol as a second stage of the reaction can occur independently. With benzyl alcohol, this stage proceeds by an ionic mechanism and leads to the formation

of the dibenzyl acetal of butynal, $CH_3-C\equiv C-CH(OCH_2C_6H_5)_2$ (III). The latter substance does not react with maleic anhydride, and its spectrum shows the presence of a triple bond. In the case of thiophenol, the second stage of the interaction with diacetylene proceeds mainly under the influence of radical initiators and results in the formation of dithio derivatives of 1,3-butadiene.

Thus, ethynylvinyl phenyl sulfide adds thiophenol or ethyl mercaptan with the formation of phenylthio- or ethylthio-1,3-butadienes according to Equation (2).

$$CH\equiv C-CH=CH-SC_6H_5 + RSH \rightarrow RS-CH=CH-CH=CH-SC_6H_5, \quad (2)$$

where R= C_2H_5 (IV); C_6H_5 (V).

The rate of this reaction is increased by KOH, azoisobutyronitrile, or increased temperature, and the yield of final products depends on the temperature and the initiator.

As in the case of ethynylvinyl ethyl sulfide [2] this reaction proceeds smoothly under the influence of radical initiators, and can be recommended for the synthesis of 1,3-phenylthioethylthiobutadienes.

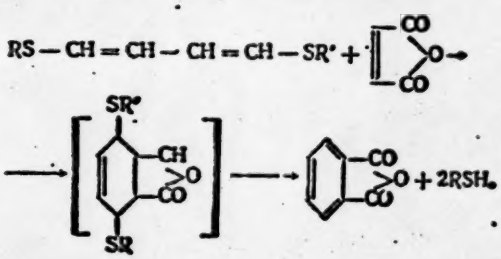
TABLE 2

Expt. No.	Mole ratio diacetylene: benzyl alcohol	Reaction temperature, °C	Yield, % of theoretical	
			ether (I)	acetal (III)
1	1: 2	80-85	16.0	—
2	1: 2	110	47.2	7.0
3	1: 15	125-135	19.8	43.6
4	1: 3	110-117	50.6	13.1

The concentration of ethynylvinyl phenyl sulfide was determined by titration with mercuric chloride in alcohol [3], a method which we previously used for ethynylvinyl ethyl sulfide [2]:

$$CH\equiv C-CH=CH-SC_6H_5 + HgCl_2 + C_2H_5OH \rightarrow C_6H_5S\cdot HgCl + \\ + HCl + (CH\equiv C-CH=CH-OC_2H_5) \quad (3)$$

The diphenylthio- and phenylthioethylthio-1,3-butadienes entered into Diels-Alder reaction with maleic anhydride forming products which lost two molecules of mercaptan under the reaction conditions with the formation of phthalic anhydride [6, 2]:



(4)

Different reaction conditions were used for the reaction of diacetylene with phenol and with p-tert-butylphenol (temperature, solvent, the presence of a stabilizer, etc.). Absorption of diacetylene was observed at 50°, and, in all cases, was accompanied by the formation of an amorphous, solid material which was insoluble in the usual organic solvents; this product was apparently the product of the further conversion of the compounds resulting

TABLE 3

Expt. No.	Weight of sulfide, g	0.1 N NaOH used, ml	Sulfide found, % of theoretical
1	0.2050	12.47	97.51
2	0.2029	12.12	95.76

from the initial reaction. The statements of a patent application [4] relating to the preparation of ethynylvinyl phenyl sulfide under the conditions used in the present work were not confirmed.

Interaction of diacetylene with thiophenol. 15.4 g of thiophenol, 0.07 g of KOH and 7.0 g of diacetylene were charged to a precooled reaction tube. With agitation, the reaction began at room temperature and the temperature rose to 40-50° due to exothermic heat. The stirring was continued for another 2 hours. After the mixture had been treated in the usual manner, distillation under vacuum gave 6.6 g (31.4% of theoretical) of ethynylvinyl phenylsulfide (II). B.p. 92.0-92.5°/2 mm; $n^{20}D$ 1.6298; d^{20}_4 1.0739; MR_D found 53.07, calculated $C_{10}H_8S$ 4# 50.22.

Found %: C 74.84; 75.06; H 5.04; 5.01; S 19.82 $C_{10}H_8S$. Calculated %: C 74.96; H 5.03; S 20.01#

6.7 g (17.7% of theoretical) of diphenylthiobutadiene (V) was also isolated; b.p. 201-202.0°/1.5 mm; m.p. 40.0-40.5°.

Found %: C 70.57; 70.40; H 5.14; 5.27; S 23.46; 23.48 $C_{16}H_{14}S_2$. Calculated %: C 71.06; H 5.21 S 23.71

The results of experiments carried out under different conditions are presented in Table 1.

Interaction of diacetylene with benzyl alcohol. 5.0 g of diacetylene was passed, over a period of 1.5 hours into a reaction tube containing a 2% solution of KOH in 32.7 g of benzyl alcohol; the reaction mixture was stirred and heated to 116-118° during the addition of the diacetylene. After an additional hour of stirring, the mixture was subjected to the usual treatment and distilled under vacuum. After distillation of the unreacted benzyl alcohol, the following fractions were collected: Fraction I, 118-120°/8 mm 8.0 g; Fraction II, 190-195°/8 mm, 3.5 g; residue 0.7 g.

Fraction I was ethynylvinyl benzyl ether (I); b.p. 104-104.5°/3 mm; $n^{20}D$ 1.5620; d^{20}_4 1.0219; MR_D found 50.25, calculated for $C_{11}H_{10}O$ 4# MR_D 48.51. The yield of the ether was 50.6% of theoretical.

Found %: C 83.57; 83.45; H 6.57; 6.44 $C_{11}H_{10}O$. Calculated %: C 83.51; H 6.37

Fraction II was the dibenzyl acetal of butynal (III); b.p. 176.5-177°/3 mm; $n^{20}D$ 1.5550, d^{20}_4 1.0696. MR_D found 79.92, calculated for $C_{18}H_{18}O_2$ #3# 79.34. The yield of the butynal acetal was 13.1% of theoretical.

Found %: C 81.18; 81.35; H 6.81; 6.79 $C_{18}H_{18}O_2$. Calculated %: C 81.18; H 6.18

Molecular weight: found 252.1; 252.6; calculated 266.3.

The results of experiments carried out under different conditions are presented in Table 2.

Interaction of ethynylvinyl phenyl sulfide with thiophenol and with ethyl mercaptan [Equation (2)]. 2.5 g of ethynylvinyl phenyl sulfide, 5.1 g of thiophenol, and 0.01 g of azoisobutyronitrile were sealed in a tube and heated at 40-50° for 4 hours, after which the contents of the tube were distilled. After distillation of the excess thiophenol, 3.95 g of substance which crystallized in the adapter was distilled; this proved to be diphenylthio-1,3-butadiene (V). B. p. 203-205°/1.5 mm; m.p. 40-40.5°.

Found %: C 70.75; 70.76; H 5.18; 5.14; S 23.77; 23.60; $C_{16}H_{14}S_2$. Calculated % C 71.06; H 5.21; S 23.71

The yield of diphenylthio-1,3-butadiene was 94.1% of theoretical.

Similarly, from 4.6 g of ethynylvinyl phenyl sulfide and 9.4 g of thiophenol, which were allowed to stand in a sealed tube at 25-30° for 20 days, was obtained 4.8 g (62.3% of theoretical based on the sulfide used) of diphenylthio-1,3-butadiene, m.p. 40-40.5°.

From 1.5 g of ethynylvinyl phenyl sulfide and 1.5 g of ethyl mercaptan in the presence of azoisobutyronitrile was obtained 1.2 g (60.0% of theoretical based on the sulfide used) of phenylthioethylthio-1,3-butadiene (IV); b.p. 166-167°/3 mm; $n^{20}D$ 1.6657; d^{20}_4 1.1097.

Literature data: b.p. 165-165.2°/2.5 mm [2].

Condensation of diphenylthio-1,3-butadiene with maleic anhydride [Equation (4)]. 1 g of diphenylthiobutadiene (obtained in the presence of nitrile), 0.4 g of maleic anhydride, and 10 ml of benzene were heated in a sealed tube for 10 hours at 130-140°. 0.45 g (85.5% of theoretical) of phthalic anhydride, m.p. 130-130.5° was obtained; a mixture with the pure compound showed no depression of the melting point.

Phthalic anhydride was also obtained, in 73.5% yield, from diphenylthio-1,3-butadiene synthesized with KOH as the initiator.

Quantitative determination of ethynylvinyl phenyl sulfide. A two-fold amount [according to Equation (3)] of a 20% solution of mercuric chloride in ethyl alcohol was added to 0.2 g of ethynylvinyl phenyl sulfide. After a day, the mixture was back-titrated with 0.1 N NaOH in the presence of Methyl orange. However, a light colored precipitate of mercuric chloride interfered with the titration.

Interaction of diacetylene with phenol and with p-tert-butylphenol. The reaction of diacetylene with phenol was carried out under a variety of conditions. In experiments carried out at temperatures up to 50° (with alkali), the original material was recovered completely. Absorption of diacetylene was observed at 50° when the reactants were mixed prior to the reaction and at 90° when the diacetylene was passed into the tube containing a base, metallic sodium, or sodium phenolate. In all cases, the reaction resulted in the formation of an amorphous, solid product in 70-80% yield based of the substance used; the product was insoluble in the usual organic solvents. The same result was obtained from the reaction of diacetylene with phenol diluted with decalin, paraffin hydrocarbon, vaseline oil, or water. The presence of p-toluidinediamine or hydroquinone had no effect on the results of the reaction.

When the reaction with p-tert-butylphenol was carried out in the presence of KOH at 40°, the diacetylene was not absorbed, and the original materials were recovered unchanged. Diacetylene was absorbed at 55-60°, and an amorphous powder (38%) was obtained.

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** Russian translation.

THE EFFECT OF HYDROGEN ON THE COURSE OF THE POLYMERIZATION OF ISOBUTYLENE OVER CATALYST FOR THE HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

Ya. T. Éidus and B. K. Nefedov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

(Presented by Academician B. A. Kazanskii, September 22, 1958)

It has repeatedly been pointed out in the past that when a mixture of hydrogen and α-olefins of normal structure is passed at atmospheric pressure and a temperature of 190° over a catalyst for the hydrocondensation of carbon monoxide with olefins (Co/clay), in addition to hydrogenation of the olefin to the corresponding paraffinic hydrocarbon, the formation of liquid hydropolymerizate proceeds to a slight extent. The yield of the latter increases with an increase in the molecular weight of the original olefin, and comprises (based on the weight of the original olefin) 0.0% for ethylene [1], 1.9% for propylene, 2.1% for 1-butene [2], 7.0% for 1-pentene [3], and 7.6% for 1-hexene [3]. In the absence of hydrogen, either no polymerizate is formed, or it is formed in an insignificant amount.

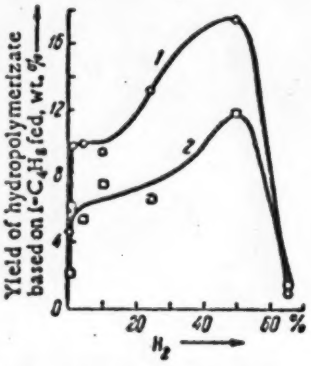

Fig. 1. Yield of liquid polymerizate, in wt. % of isobutylene fed, at initial (1) and stabilized (2) activity.

It has been proposed [5] that during the interaction of an olefin with hydrogen under the indicated conditions, alkyl radicals (half-hydrogenated forms of the olefins) are formed on the surface of the catalyst as intermediate products; these radicals can initiate the polymerization reaction.

The present work was carried out with the aim of investigating the process of the polymerization of isobutylene and the effect of hydrogen on this process under the same conditions.

EXPERIMENTAL

The apparatus and experimental method were the same as those described previously in reference [6]. The catalyst used was a precipitated Co/clay (1 : 2) catalyst [7] usually used for the hydrocondensation of carbon monoxide with olefins and for the hydropolymerization of olefins under the influence of small amounts of cargon monoxide [8]. The catalyst was reduced with electrolytic hydrogen at 450° for 5 hours, and was regenerated in a similar manner. For comparison, fire clay, preliminarily calcined at 450°in a stream of air [7], was tested as a catalyst; this clay was used as the support for the Co catalyst. The volume of each catalyst sample was 30 cc. The glass reaction tube had a diameter of 10 mm. The isobutylene feed was obtained by dehydration of isobutyl alcohol (b.p. 107-108°; $n^{20}D$ 1.3957; d^{20}_4 0.8019) over aluminum oxide, and was purified by twice condensing under vacuum. After purification, the content of carbon monoxide did not exceed 0.02%, and other impurities amounted to 1-2%. All experiments were carried out at atmospheric pressure, a temperature of 190°, and a space rate of feed gas of ~100 hour^{-1}.

TABLE 1

Expt. no.	Feed gas comp., vol. %		Run time, hours	Isobutylene reacted, %	Hydrogen reacted, %	Yield of liquid polymerizate, wt. %	
	isobutylene	hydrogen				of isobutylene fed	of isobutylene reacted
			Co/clay catalyst				
1	98,8	0,0	5	4,7	—	4,7	100
2	98,8	0,0	16	2,3	—	2,3	100
3	98,8	0,2	5	23,4	100	10,1	43,2
4	98,8	0,2	10	6,9	100	6,3	91,3
5	95,0	4,0	5	26,0	100	10,1	38,8
6	95,2	3,8	16	7,8	100	5,6	71,6
7	89,0	10,0	5	(12,5)	100	9,5	(76,0)
8	88,3	10,8	15	9,1	100	7,9	86,8
9	76,2	23,0	6	42,0	100	13,5	32,1
10	74,0	25,3	15	19,9	96,8	6,7	33,7
11	50,0	49,2	5	90,7	97,5	17,9	19,7
12	48,5	50,1	10	79,1	100	12,0	15,1
13	34,0	65,0	5	93,0	64,0	1,0	1,1
14	34,1	64,7	10	98,3	60,5	1,8	1,9
			Clay catalyst				
15	73,8	25,4	5	27,7	—	21,5	77,6
16	72,5	26,4	10	13,3	—	13,3	100
17	99,8	0,0	5	26,3	—	25,2	95,8
18	99,8	0,0	10	14,4	—	14,3	99,3
19	99,8	0,0	5	41,9	—	31,4	74,9
20	99,8	0,0	6	15,7	—	15,7	100

Notes: 1) In Experiments 3, 5, 7, 9, 11, and 13, the catalyst was regenerated before the experiment. Moreover, in Experiments 7, 11, and 13, the freshly reduced catalyst was contacted with the feed gas at a temperature of 190°. 2) Catalyst No. 2 was used in Experiments 15-18 and Catalyst No. 3 in Experiments 19 and 20.

Experiments with Co/clay catalyst. In Table 1 and Figures 1 and 2 are presented the results of experiments carried out with isobutylene and isobutylene–hydrogen mixtures over Co/clay catalyst. The same sample of catalyst was used in these experiments; it was regenerated before each change in composition of the feed mixture. Freshly precipitated as well as freshly regenerated catalyst had an activity approximately twice that established 10-15 hours after the beginning of the run. These activities have been denoted conventionally by the terms "initial" and "stabilized". As seen from Table 1 and Figure 1, isobutylene polymerized to an extent of 5% at initial activity and 2% at stabilized activity. The addition of 0.2% H_2 caused an increase in yield by a factor of 2-2.5. In the concentration interval of 0.2-10% H_2, the yield of hydropolymerizate remains constant, while an increase in the concentration of H_2 to 50% increased the yield to 18 and 12%, respectively, for initial and stabilized catalyst. At H_2 concentrations above 50%, the yield of hydropolymerizate decreased sharply. The fraction of isobutylene reacting continuously increased with an increase in the hydrogen concentration in the feed gas; however, this increase was due to an increase in hydrogenation reactions – the yield of hydropolymerizate based on reacted isobutylene continuously decreased, and the amount of hydrogen reacted increased (Table 1).

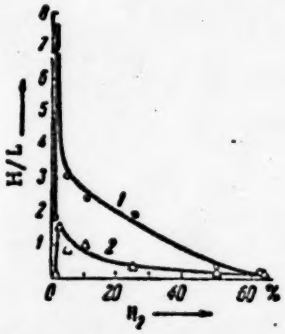

Fig. 2. Ratio of heavy (H) to light (L) oil at initial (1) and stabilized (2) activity.

It is interesting to note that with the addition of 0.2% H_2 to the isobutylene there was a sharp increase in the ratio of th heavy fraction of the polymerizate (H) to the light (L), and then, with an increase in the concentration of H_2 in the feed gas, this ratio gradually decreased (Figure 2). Hydrocracking occurred simultaneously with hydrogenation, as is apparent from,

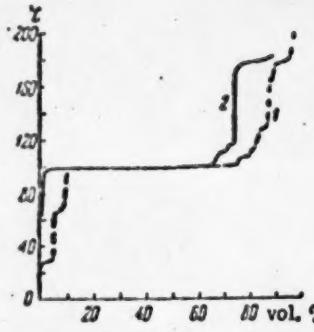

Fig. 3. Distillation curves of the hydrogenated hydropolymerizate obtained with Co/clay catalyst (1) and hydrogenated isobutylene polymerizate obtained with clay (2).

for example, the significant increase in the amount of C_1-C_3 hydrocarbons in the effluent gas. Thus, the effluent gas in Experiment 9 contained (in volume percent) 0.0% CO_2, 37.0% H_2, 19.0% CH_4, 1.6% C_2H_6, 0.0% C_2H_4, 3.7% C_3H_8, 32.5% $i\text{-}C_4H_{10}$, 0.6% $i\text{-}C_5H_{12}$, and 4.4% air.

About 100 ml of hydropolymerizate ($n^{20}D$ 1.4083, d^{20}_4 0.7041, bromine number 111.3, unsaturates content 77.8%) was obtained in a long run with a feed mixture containing 75% isobutylene and 25% hydrogen; this was hydrogenated at room temperature in the presence of Pt on carbon promoted with H_2PtCl_6 [9]. The resulting hydrogenation product ($n^{20}D$ 1.3979, d^{20}_4 0.6909, bromine number 0.0) was distilled in a column packed with triangular copper spirals and having an efficienty of 40 theoretical plates. It is apparent from the distillation curve (Fig. 3, 1) that the hydrogenation product consisted of ~60% isobutylene hydrodimer 2,2,4-trimethylpentane (b.p. 99.0-99.2°/760 mm, $n^{20}D$ 1.3915, d^{20}_4 0.6917, literature data: b.p. 99.24°, $n^{20}D$ 1.3915, d^{20}_4 0.6919); it also contained hydrotrimer as well as C_5 and C_6 fractions, the presence of which indicates the occurrence of hydrocracking.

In order to clear up the question of whether the increase in the yield of isobutylene polymerizate with the addition of 0.2% and more hydrogen is not caused by regeneration of the contact surface by the hydrogen, a gaseous mixture of N_2 + 0.3% H_2 was passed for 5 hours over the Co/clay catalyst at 190° after experiments on the polymerization of isobutylene (Figure 4, 1, a). As a result of this treatment, future yields of polymerizate not only were not increased, but were even significantly decreased (1, b). The polymerization activity increased when the catalyst was treated at 190° with a $3N_2:1H_2$ mixture, and increased still more when the ratio was $1N_2:1H_2$ (1, c and d). When isobutylene containing 0.3% H_2 was polymerized, the yield of polymerizate increased without preliminary treatment of the catalyst with hydrogen-containing gas, as was observed earlier in Experiments 3 and 4 of Table 1.

Experiments with clay as the catalyst. In Table 1 are presented the results of experiments in which the support—clay—for the previous catalyst was used as the catalyst. In this case also, an initial and a stabilized activity were observed. Isobutylene polymerization amounted to 25-30 and 14-16%, respectively. Ethylene was not polymerized under these conditions. The addition of 25% H_2 to the isobutylene brought about a small decrease in the yield of polymerizate to 21.5 and 13.3% for the initial and stabilized catalysts, respectively.

60 ml of polymerizate ($n^{20}D$ 1.4180, d^{20}_4 0.7203) was obtained in a long run with isobutylene; this was hydrogenated by the above method [9], and the resulting hydrogenation product ($n^{20}D$ 1.4000, d^{20}_4 0.6976) was distilled in the same column. It is apparent from the distillation curve (Figure 3, 2) that the hydrogenation product boiled in the range 63-180° and consisted of 80% isobutylene hydrodimer, which contained up to 90% 2,2,4-trimethylpentane.

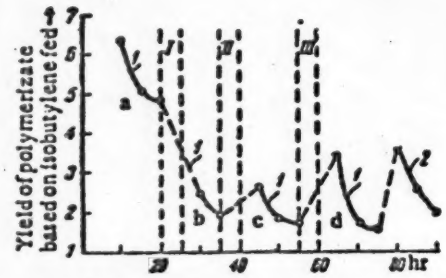

Fig. 4. Effect on catalyst activity of treatment of Co/clay catalyst with mixtures of N_2 + 0.3% H_2 (I), 75% N_2 + 25% H_2 (II), and 50% N_2 + 50% H_2 (III). 1) Polymerization of isobutylene; 2) polymerization of a mixture of isobutylene + 0.3% H_2. See text for remaining notation.

The resulting show that in the presence of catalyst for the hydrocondensation of carbon monoxide with olefins, Co/clay, isobutylene polymerizes to the extent of 2-5% in contrast to n-butylenes, which do not polymerize over this catalyst [10]. Of particular interest are the data obtained in the present work showing that the addition of hydrogen to isobutylene has a substantial effect on the polymerization process; even a small addition of hydrogen, 0.2%, causes a significant increase in the yield of polymerizate and an increase in the depth of conversion. An increase in the H_2 concentration from 10 to 50% causes a further increase in the yield of polymerizate and an increase in the side processes of hydrogenation and hydrocracking. It must be pointed out that if the increase in polymerization with the addition of 10-50% hydrogen to the isobutylene were due to a certain extent to partial

regeneration of the catalyst surface, then as shown by the experiments discussed above, the sharp jump in the yield of polymerizate with the addition of 0.2-0.3% H_2 could not be so explained and must obviously be ascribed to the intermediate formation on the catalyst surface of isobutyl radicals – half-hydrogenated isobutylene – which, by taking part in the polymerization process, exert an accelerating effect on this process.

The effect of hydrogen on the course of the polymerization was observed only in the case of Co catalyst. Hydrogen exerts no such effect on the support for this catalyst – clay – which is a considerably more active catalyst for the polymerization of isobutylene than is Co/clay catalyst; in this case, the hydrogen is merely a diluent. This could indicate that radicals are not formed on the surface of the clay, so that the polymerization proceeds exclusively by an ionic mechanism with the formation mainly of dimer and trimer. Over Co/clay catalyst, the process apparently has a mixed character and proceeds partly by an ionic and partly by a radical mechanism.

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RECOVERY OF PENTAVALENT NEPTUNIUM BY EXTRACTION

Corresponding Member AN SSSR I. P. Alimarin,
Yu. A. Zolotov and E. S. Pal'shin

V. I. Verdanskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR

Up to the present, there has been no reliable information on the extraction of pentavalent neptunium. Kool [1, 2] studying the extraction of Np (V) from nitric acid solutions with methyl isobutyl ketone and other solvents, came to the conclusion that there is significant extraction of neptunium at nitric acid concentrations above 5-6 M. However, pentavalent neptunium disproportionates to a considerable extent under these conditions, and the products of the disproportionation reaction – Np (IV) and Np (VI) – are readily extracted by oxygen-containing solvents. In this connection, the author's results require confirmation with macro amounts of Np^{237}. Nor are there data on the extraction of other pentavalent actinides which form ions of the type MeO_2^+ i. e., uranium, plutonium and americium.

In the present work, it was shown that pentavalent neptunium is extracted by solutions of 1-nitroso-2-napthol in n-butyl and isoamyl alcohols at a pH of 9-10.

The present investigation was carried out on tracer amounts of Np^{239}, and the results were confirmed with weighable amounts of Np^{237}. The Np^{239} isotope was separated from neutron-irradiated uranium by a method based on recoil of the nuclear fission products [3] and was identified by its half-life. The activity was measured by the usual end window counter with an accuracy of ± 5%.

The initial solutions of neptunium (V), which were obtained by reduction of neptunium (VI) with hydrazine in the cold, were brought to the predetermined pH by means of ammonia and nitric acid; buffer solutions were not used in order to avoid possible complex formation of the neptunoyl ion with components of the buffer mixtures. The pH measurements were carried out potentiometrically. The extractions were carried out in graduated test tubes with ground-glass stoppers; the neptunium was extracted from a volume of 2 ml by an equal volume of a 1% solution of 1-nitroso-2-naphthol in the appropriate solvent. The mixtures were agitated for 4 minutes. The experimental conditions were selected taking into consideration the previously obtained data on the extraction of uranyl with 1-nitroso-2-naphthol [4].

Solutions of the reagent in solvents belonging to various classes of organic compounds were used: benzene, chloroform, isoamyl alcohol, n-butyl alcohol, diethyl ether, amyl acetate, and methyl ethyl ketone.

The results obtained are present in Figure 1.

It follows from these data that neptunium is not extracted at a pH up to 6; with a further increase in the pH, transfer of a considerable fraction of the neptunium to the organic phase is observed. Extraction is especially good at a pH of 8-10. The percent extraction depends strongly on the nature of the solvent; n-butyl alcohol extracts more than 90-95% of the neptunium in a single step, isoamyl alcohol extracts 80-85%, and methyl ethyl ketone, chloroform, and amyl acetate are considerably worse; when benzene or diethyl ether is used, there is almost no extraction. As may be readily seen, n-butyl alcohol has the great pH interval for extraction.

In the case of the majority of solvents, precipitation of the 1-nitroso-2-naphthol occurs at a pH above 9-10. The reagent does not precipitate from n-butyl alcohol at a pH of up to 11.4.

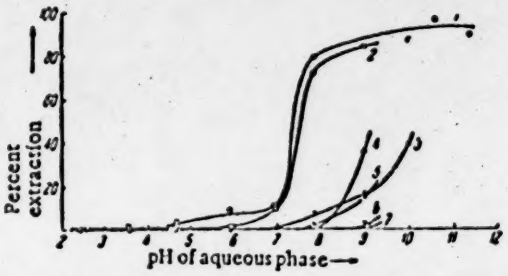

Fig. 1. Extraction of pentavalent neptunium by solutions of 1-nitroso-2-naphthol in various solvents: 1) n-butyl alcohol; 2) isoamyl alcohol; 3) chloroform; 4) methyl ethyl ketone; 5) amyl acetate; 6) benzene; 7) diethyl ether.

A decrease in the concentration of the reagent in n-butyl and isoamyl alcohols to 0.25% broadens the pH interval for the extraction and improves phase separation.

Significant amounts of fluorides, carbonates, phosphates, acetates, and citrates interfere with the extraction of plutonium; the extraction is strongly depressed by ethylenediaminetetraacetic acid; small amounts of carbonates and fluorides have almost no effect. Nitrates, chlorides, and sulfates do not interfere with the extraction.

On the basis of these results, it must be emphasized, first of all, that the extraction of neptunium indicates an interaction of the NpO_2^+ ion with 1-nitroso-2-naphthol. This fact is interesting by itself. The literature reports no known reaction of pentavalent neptunium with organic reagents, provided the appreciable complex formation with oxalic [5] and certain other [6] organic acids is ignored; there are no analytical reactions for pentavalent neptunium. As is well known, the properties of oxygen-containing ions of pentavalent actinides have not been sufficiently studied, generally speaking.

That the NpO_2^+ ion interacts with 1-nitroso-2-naphthol, which has an OH^- group, is in agreement with the previously observed [6] change in the absorption spectra of pentavalent neptunium solution containing certain carboxylic acids and phenols, which was considered to be proof of complex formation (the absorption spectra changed at a pH of about 6). Consideration of these data opens up a route for the search for analytical reaction for the determination of plutonium in its most stable valence state. It is obvious that the preferential reaction of the neptunoyl ion with organic reagents containing an OH^- group proceeds at extremely high pH values corresponding to the pH for the beginning of hydrolysis of pentavalent neptunium. These values apparently lie in the pH interval 6-10. Such a conclusion is tantamount to considering the neptunoyl ion as a large, singly charged ion with a low polarizing action.

Our data can be used in the separation of neptunium from plutonium and uranium. Extraction of uranyl 1-nitroso-2-naphtholate takes place at a pH above 3.5-4.0 [4]; neptunium (V) remains in the aqueous phase under these conditions. The extraction of plutonium in the tetravalent state, as we, together with D. Nishanov, have established, takes place at a pH of 1.0-1.5. The possibility of obtaining in a single solution hexavalent uranium, pentavalent neptunium, and tetravalent plutonium (this is accomplished, for example, by the action of sodium nitrite) opens up the possibility of separating these elements. Investigations continue along this line.

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SYNTHESIS OF FERROCENE DERIVATIVES BY MEANS OF N,N-DIMETHYLAMINOMETHYLFERROCENE METHIODIDE

A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva and Yu. A. Ustynyuk

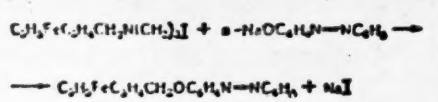
M. V. Lomonosov Moscow State University

First prepared by Hauser and Lindsay [1], N,N-dimethylaminomethylferrocene methiodide, like trimethylbenzylammonium iodide in other syntheses, has proved to be a convenient reagent for the introduction of the ferrocenylmethyl group [2-8].

We have previously used N,N-dimethylaminomethylferrocene methiodide for the synthesis of methylferrocene [5]. In the present work, we carried out certain reactions in which the dimethylamino group was substituted as well as the aminomethylation and aminoethylation of ferrocene.

Thus, by the interaction of N,N-dimethylaminomethylferrocene methiodide with sodium sulfite, we obtained the sodium salt of ferrocenylmethanesulfonic acid, while reaction with potassium thiocyanate gave ferrocenylmethyl thiocyanate. Sodium phenolate and

β-naphtholate formed the phenyl and β-naphthyl ethers of ferrocenylcarbinol. Ferrocenylmethylation of p-hydroxyazobenzene gave an azo-compound containing a ferrocenyl group. Attempts to synthesize an

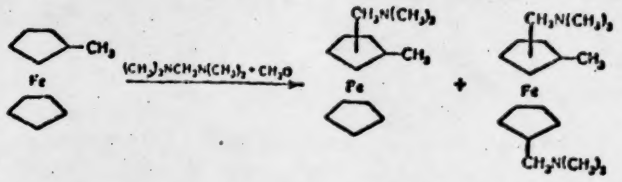


azo compound with a ferrocenyl group have been unsuccessful until now, since ferrocene is acetylated during reactions with diazo compounds, and reaction of nitrous acid with ferrocene and its derivatives give a brown compound of unknown structure which is insoluble in organic solvents, acids, and bases. Thus, for example, we were unable to diazotize p-ferrocenylaniline.

By aminomethylation of methylferrocene [5] with a mixture of N,N,N',N'-tetramethyldiaminomethane and paraformaldehyde, we obtained a 60% yield of homoannular (N,N-dimethylaminomethyl)methylferrocene (the presence of an unsubstituted ring was shown by the infrared spectrum).

Thus, aminomethylation of methylferrocene occurs in the substituted cyclopentadienyl ring with a yield somewhat higher than with ferrocene, which aminomethylates with a yield of 51% under the same conditions [2].

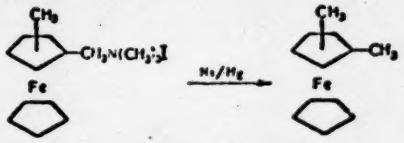
The addition of phosphoric acid to the reaction mixture leads, as in the case of ferrocene [8], to an increase in the yield of (N,N-dimethylaminomethyl)methylferrocene to 80%; moreover, diaminomethylated ferrocene is obtained in 10% yield.



An increase in the heating time increases the yield of di(N,N-dimethylaminomethyl)methylferrocene to 32% and a decrease in the yield of monoaminomethylated methylferrocene to 42%.

In no case of aminomethylation of ferrocene were we able to isolate diaminomethylation products. Special experiments also showed that the aminomethylation of N,N-dimethylaminomethylferrocene does not proceed under conditions of the Mannich reaction for ferrocene nor by the introduction of an excess of the aminomethylating agent and an increase in the heating time.

Consequently, the methyl group in methylferrocene strongly activates the ferrocene nucleus with respect to electrophilic attack. The formation of homoannular (N,N-dimethlaminomethyl)methylferrocene indicates the ring connected to the methyl group is the more strongly activated. The formation of dimethylaminomethylated methylferrocene is one more bit of evidence that the effect of substituents is transmitted from one cyclodienyl ring to the other through the iron atom [9]. From (N,N-dimethylaminomethyl)methylferrocene methiodide we synthesized homoannular dimethylferrocene.



A comparison of the infrared spectra of the dimethylferrocene and (N,N-dimethylaminomethyl)methylferrocene with homoannularly substituted ferrocenes of known structure indicated that the alkyl groups were in the 1- and 3-positions.

EXPERIMENTAL

Sodium ferrocenylmethanesulfonate $C_5H_5 \cdot FeC_5 \cdot H_4CH_2SO_3Na \cdot H_2O$. This compound was prepared as previously described for dimethylbenzylphenylammonium chloride [10]. A solution of 1.1 g (0.003 mole) of N,N-dimethylaminomethylferrocene methiodide and 1.5 g (0.006 mole) of $Na_2SO_3 \cdot 7H_2O$ in 60 ml of water was heated for 7 hours at 70-80°; an aqueous solution of $Ba(OH)_2$ was then added and the excess barium ions were removed by passing CO_2 through the mixture. The precipitate was filtered and washed with a small amount of water. The filtrate was evaporated to a small volume (5-6 ml). The precipitated sodium salt of ferrocenylmethanesulfonic acid was filtered (weight 0.7 g, yield 77% of theoretical) and recrystallized from water and then from alcohol; it did not melt at temperatures up to 230°; it crystallized with one molecule of water.

Found %: C 41.51; 41.63; H 4.05; 4.26 $C_{11}H_{13}FeSO_4Na$. Calculated %: C 41.29; H 4.09

Ferrocenylmethyl thiocyanate, $C_5H_5FeC_5H_4CH_2SCN$. An aqueous solution of 0.3 g (0.0031 mole) of potassium thiocyanate was poured into an aqueous solution of 0.37 g (0.0001 mole) of N,N-dimethylaminomethylferrocene methiodide. The mixture was heated at the boiling point for 3 hours. When the mixture was cooled and acidified with dilute, 1:1, hydrochloric acid, a yellow precipitate of ferrocenylmethylthiocyanate formed (weight 0.13 g, yield 46% of theoretical). Recrystallization from petroleum ether gave a product with an m.p. of 59-61°.

Found %: C 55.95; 55.87; H 4.32; 4.45; Fe 21.88; 21.54; S 12.18; 12.01; N 5.32; 5.12 $C_{11}H_{11}FeSN$.
Calculated %: C 55.90; H 4.31; Fe 21.72; S 12.47; N 5

Phenyl ether of ferrocenylcarbinol, $C_5H_5FeC_5H_4 \cdot CH_2OC_6H_5$. An aqueous solution of 0.30 g (0.0008 mole) of N,N-dimethylaminomethylferrocene, 0.1 g (0.001 mole) of phenol, and 0.05 g (0.001 mole) of NaOH was heated for 5 hours at 80-90°, during which time a brown precipitate formed. The mixture was then extracted with ether.

The ether solution was washed with 5-7% NaOH and then with water, and was dried with calcined Na_2SO_4. Evaporation of the ether under vacuum gave 0.2 g (80% of theoretical) of the phenyl ether of ferrocenylcarbinol. M.p. 129-130° (recrystallized from petroleum ether).

Found %: C 69.94; 69.90; H 5.87; 6.01; Fe 19.36; 19.20 $C_{17}H_{16}FeO$. Calculated %: C 69.87 H 5.51; Fe 19.15

β-Naphthol ether of ferrocenylcarbinol, $C_5H_5FeC_5H_4CH_2OC_{10}H_7$-β. This ether was prepared in a manner similar to that used for the phenyl ether. The yield was 40% of theoretical. It was recrystallized from petroleum ether, m.p. 121-123° with decomposition (in a sealed capillary).

Found %: C 73.35; 73.48; H 5.71; 5.73; Fe 15.85; 15.76; $C_{21}H_{18}FeO$. Calculated %: C73.69; H 5.30 Fe 16.32

p-(Ferrocenylmethoxy)azobenzene, $C_5H_5FeC_5H_4CH_2 \cdot OC_6H_4N=NC_6H_5$.* An aqueous solution of 1 g (0.003 mole) of N,N-dimethylaminomethylferrocene was added to a solution of 0.5 g (0.003 mole) of p-hydroxyazobenzene in 5% sodium hydroxide. The mixture was heated fro 20 hours at 90-100°. The resulting precipitate of for p-(ferrocenylmethoxy)azobenzene was filtered, washed repeatedly with 5% NaOH and with water, dried in a vacuum dessicator over P_2O_5 (weight 0.8 g, yield 80% of theoretical), and recrystallized from benzene. M.p. 135.5-137.5° (in a sealed capillary).

Found %: C 69.93; 70.01; H 5.35; 5.34; Fe 14.18; 14.15; N 6.96; 7.00 $C_{23}H_{20}FeON_2$. Calculated %: C 69.71; H 5.09; Fe 14.09; N 7.07

N,N-Diethylaminomethylferrocene methiodide, $C_5H_5FeC_5H_4CH_2N(C_2H_5)_2(CH_3)I$. 6.4 g of paraformaldehyde was dissoved, with heating, in a mixture of 20.8 g (0.2 mole) of $(C_2H_5)_2NH$ and 50 ml of glacial acid, and 18.6 g (0.1 mole) of ferrocene was then added. The reaction mixture was heated for 16 hours at 80-100°, after which it was diluted with water, and the unreacted ferrocene was filtered and washed with dilute HCl. The weight of unreacted ferrocene was 16.8 g.

The aqueous solutions were combined and washed with water to remove the residual ferrocene, made alkaline, and again extracted with ether. Distillation of the ether gave 2 g of an oily material, from which the diethylaminomethylferrocene was steam distilled (soft, bright yellow crystals); this was converted to the methiodide by reaction with an ether solution of CH_3I. The methiodide was recrystallized from alcohol, and it melted with decomposition at 159-162°, beginning to darken at 153-155°.

Found %: C 46.50; 46.61; H 6.15; 5.77; Fe 13.40; 13.66; I 30.63; 31.16; N 4.00; 4.10 $C_{16}H_{24}FeNI$. Calculated %: C 46.50; H 5.85; Fe 13.52; I 30.72; N 3.38

(N,N-Dimethylaminomethyl)methylferrocene, $C_5H_5 \cdot FeC_5H_3(CH_3)CH_2N(CH_3)_2$. Aminomethylation of methylferrocene was carried out with bis(dimethylamino)-methane in the presence of H_3PO_4 in the manner described previously ferrocene [8]. A mixture of 30 g (0.15 mole) of methylferrocene, 15.3 g (0.15 mole) of bis(dimethylamino) methane, 4.5 g (0.15 mole) of paraformaldehyde, 30 g of H_3PO_4 (sp. gr. 1.73), and 200 ml of glacial CH_3COOH was heated for 7 hours at 95°.

The reaction products were vacuum distilled in a stream of N_2 over Zn dust. 31 g (yield 80% of theoretical) of (N,N-dimethylaminomethyl)methylferrocene was obtained. B. p. 115-118°/1 mm; 138-140°/5 mm; $n^{20}D$ 1.5812; d^{20}_4 1.2150.

Found %: C 65.49; 64.31; H 7.61; 7.64; Fe 21.20; 21.53; $C_{14}H_{19}NFe$. Calculated %: C 65.38; H 7.45 Fe 21.71

Infrared spectrum:(NaCl prism) 740, 798, 846; 928; 950; 1004; 1040; 1106; 1140; 1176; 1232; 1254; 1266; 1354; 1380, 1454; 1466; 1660; 1682 cm^{-1}.

Moreover, there was obtained 4.7 g (yield, 19% theoretical) of di(N,N-dimethylaminomethyl)methylferrocene. B. p. 130-131.5°/1 mm; $n^{20}D$ 1.5622; d^{20}_4 1.1260.

Found %: C 65.64; 65.53; H 8.62; 8.42; N 8.90; 9.08; Fe 17.16; 17.11; $C_{15}H_{26}N_2Fe$. Calculated %: C 64.96; H 8.35; N 8.94; Fe 17.77

*Prepared in couperation with A. A. Ponomarenko.

Infrared spectrum: 741; 790; 849; 936; 954; 1024; 1038; 1146; 1174; 1268; 1354; 1460 cm^{-1}. (NaCl prism).

(N,N-dimethylaminomethyl)methylferrocene methiodide, which was prepared in absolute methyl alcohol (ice cooling) followed by precipitation with ether, decomposed when heated above 185°.

Found %: C 45.18; 45.08; H 5.61; 5.78; N 3.83; 3.95; Fe 13.25; 13.48 $C_{15}H_{22}NFeI$. Calculated %: C 45.15; H 5.57; N 3.51; Fe 13.99

When methylferrocene was aminomethylated without the addition of H_3PO_4, (N,N -dimethylaminomethyl)-methylferrocene was obtained in 60% yield (if recovered as the methiodide, the yield reached 70%).

When the aminomethylation of methylferrocene was carried out at 110-115° for 10 hours, the yield of di(N,N-dimethylaminomethyl)-methylferrocene amounted to 32% of theoretical, and (N,N-dimethylaminomethyl)-methylferrocene was obtained in 42% yield.

Dimethylferrocene $C_5H_5FeC_5H_3(CH_3)_2$. This compound was prepared by reduction of (N,N-dimethylamino-methyl)methylferrocene methiodide with sodium amalgam in a manner similar to that used for the preparation of methylferrocene [5].

The dimethylferrocene was purified chromatographically over Al_2O_3 and by vacuum distillation. The yield was 75%. B.p. 77°/4 mm; 119°/13 mm; $n^{20}D$ 1.6007; $n^{35}D$ 1.5922; d^{20}_4 1.2458.

Found %: C 66.91; 67.10; H 6.54; 6.57; Fe 26.37; 26.34; $C_{12}H_{14}Fe$. Calculated %: C 67.28; H 6.50; Fe 26.08

Infrared spectrum: 748; 754; 776; 926; 950; 1002; 1040; 1106; 1210; 1236; 1280; 1322; 1384; 1460; 1650 cm^{-1}. (NaCl prism).

The absorption in the regions of 1000 and 1100 cm^{-1} shows that (N,N-dimethylaminomethyl)methylferro-cene are homoannular, and the presence of the 1266 and 1280 cm^{-1} frequencies, respectively, indicated that the substituents are in the 1- and 3-positions. •

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• The 1,2-(N,N-dimethylaminomethyl)methylferrocene described by Hauser and co-workers [3] was actually β-ferrocenylethyldimethylamine [6, 8, 11, 12].

•• Original Russian pagination. See C. B. Translation.

THE EFFECT OF SIDE CHAINS ON THE RATE OF OXIDATION OF CARBON-CHAIN POLYMERS

V. M. Yur'ev, A. N. Pravednikov and Academician S. S. Medvedev

L. Ya. Karpov Physicochemical Scientific Research Institute

The following reactions are basic in the oxidation of hydrocarbons: addition of a molecule of oxygen to a hydrocarbon radical

$$R\cdot + O_2 \rightarrow ROO\cdot; \quad (1)$$

removal of a hydrogen atom by a peroxy radical from a hydrocarbon molecule with the formation of a hydroperoxide group

$$ROO\cdot + RH \rightarrow ROOH + R\cdot; \quad (2)$$

decomposition of the hydroperoxide group with the formation of HO· and RO· radicals

$$ROOH \rightarrow RO\cdot + \cdot OH; \quad (3)$$

removal of a hydrogen atom by these radicals from molecules of hydrocarbon

$$\begin{matrix} RO\cdot + RH \rightarrow ROH + R\cdot, \\ \cdot OH + RH \rightarrow H_2O + R\cdot. \end{matrix} \quad (4)$$

The rates of all of these elemental reactions determine the rate of the hydrocarbon oxidation process.

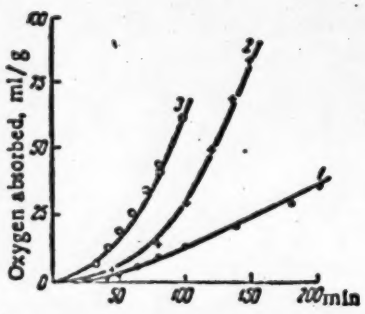


Fig. 1. Absorption of oxygen by polymethylene and other aliphatic polymers at 150°. 1) Polymethylene (mol. wt. 437,000); 2) polymer prepared by decomposition of a mixture of 75 mol.% diazomethane and 25 mol.% diazoethane (mol. wt. 440,000); 3) polymer prepared by decomposition of a mixture of 75 mol.% diazomethane and 25 mol.% diazobutane (mol. wt. 668,000).

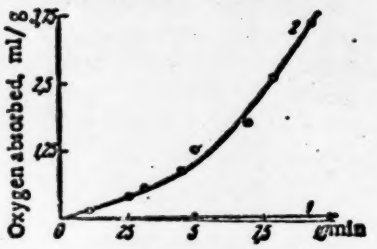


Fig. 2. Absorption of oxygen by polystyrene and poly-p-isopropylstyrene at 205°. 1) Polystyrene (mol. wt. 700,000); 2) poly-p-isopropylstyrene (mol. wt. 3120; isopropyl group content ~100%).

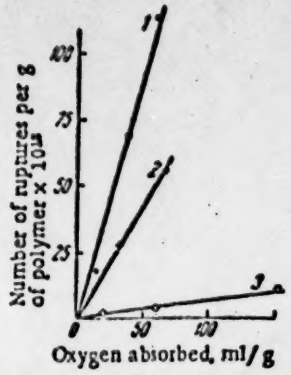


Fig. 3. Relationship between the number of ruptures per gram of polymer and the amount of oxygen absorbed during the oxidation of aliphatic polymers at 150°. Notation is the same as in Figure 1.

It is well known that on going from low-molecular weight to high molecular weight compounds of similar structure there is observed an appreciable decrease in the rate of oxidation. Thus, for example, isopropylbenzene oxidizes very readily, while its polymer analog, polystyrene, is oxidized with great difficulty [1, 2]. Such a decrease in the rate of oxidation of polymers can be explained as follows. The removal of an atom of hydrogen from the hydrocarbon molecule [Reactions (2) and (4)] is connected with a transition of the corresponding portion of the molecule from a tetrahedral to a planar configuration. In the case of polymers, this transition is connected with a displacement of portions of the polymer chain, which must lead to an increase in the activation energy of the reaction and, consequently, to a decrease in reaction rate (in comparison with the activation energies and rates of similar reactions of low-molecular weight compounds).

The removal of a hydrogen atom from a side chain (methyl, propyl, etc.) is not connected with shifting of portions of the polymer chain in the transition state, and must have the same activation energy as the corresponding reactions of low-molecular-weight compounds. Therefore, it would be expected that in the case of polymers containing comparatively short side chains, oxidation will take place primarily at the side chains.

With the aim of confirming this assumption, we synthesized polymethylene and polymers containing methyl and propyl side chains (by the decomposition of diazomethane or mixtures of the appropriate diazocompounds in the presence of BF_3 [3]) and polyisopropylstyrene (by alkylation of polystyrene with isopropyl chloride in the presence of $AlCl_3$ [4]).

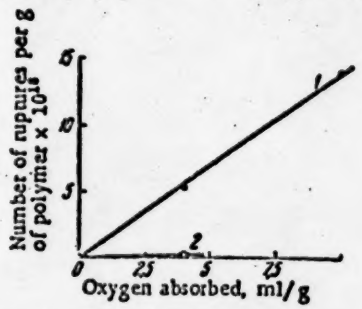
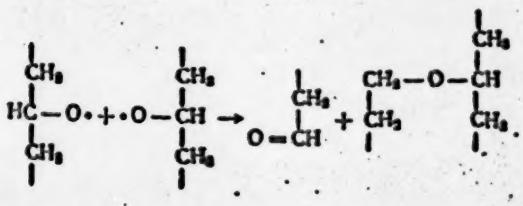


Fig. 4. Relationship between the number of ruptures per gram of polymer and the amount of oxygen absorbed during the oxidation of polystyrene and poly-p-isopropylstyrene at 205°. Notation is the same as in Figure 2.

Experiments on the oxidation of these polymers showed that the introduction of side chains sharply increases the rate of absorption of oxygen (Figures 1 and 2), and, simultaneously, there was an increase in the number of molecules of oxygen consumed per rupture of the main chain (Figures 3 and 4); i.e. oxidation actually proceeded chiefly at the side chains in this case.

When the polymers obtained by decomposition of diazo compounds and the poly-p-isopropylstyrene were oxidized to a greater extent (100-150 ml of O_2 per g of polymer for polymethylene, etc. and 5-10 ml of O_2 per g of polymer for poly-p-isopropylstyrene) linking of the polymer chains occurred as a result of the formation of ether bridges (determined by infrared spectra) between the macromolecules (cf. also [5]), and a very low molecular weight fraction appeared in the system. It is possible that these changes are connected with the occurrence of a bimolecular reaction involving two oxygen-containing radicals according to [6]:



Polystyrene is not cross-linked when oxidized to an extent of up to ~20 ml of O_2 per g of polymer, and this is apparently explained by the low concentrations of radicals in the system (low rate of oxidation).

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THE ADDITION OF SULFUR TRIOXIDE TO FLUOROOLEFINS

M. A. Dmitriev, G. A. Sokol'skii and Academician
I. L. Knunyants

In spite of the accumulated ideas regarding the difficulty of adding strongly electrophilic reagents to (polyfluoro) olefins, it was found that sulfur trioxide adds comparatively readily to tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene. Depending on the sulfur trioxide modification used, the initially formed reaction products are β-sultones (in the case of the α-modification) or β-pyrosultones (in the case of sulfur trioxide dimer). The way in which the sulfur trioxide added across the double bond of the unsymmetrical fluoroolefins was determined by acidometric titration of the addition products and determination of the hydrolyzable halide. The cyclic addition products formed and some of their physical properties are presented in Table 1.

TABLE 1

Prep. no.	Formula	B.p., °C	d_4^{20}	n_D^{20}	MR found	MR calc.
1	$CF_2-CF_2-SO_2$ (O)	33	1,6219	1,3050	21,07	20,80
2	$CF_2-CF_2-SO_2-O-SO_2$ (O)	105—106	1,7407	1,3470	31,38	31,29
3	$CF_2-CFCl-SO_2$ (O)	77—78	1,7269	1,3670	25,56	25,63
4	$CF_2-CFH-SO_2$ (O)	104—105	1,7082	1,3530	20,58	20,72
5	$CF_2-CF(CF_3)-SO_2$ (O)	42—43	1,6570	1,3000	26,42	26,05

The products of the reaction of sulfur trioxide with fluoroolefins are extremely reactive compounds, and they interact vigorously with representatives of different classes of organic and inorganic substances. In the vast majority of cases, these reactions result in derivatives of fluorine-containing α-fluorosulfonylcarboxylic acids. Thus, the interaction of tetrafluoroethane-β-sultone (sultone of 2-hydroxyethanesulfonic acid) with water gave fluorosulfonyldifluoroacetic acid, while reaction with alcohols, mercaptans, and amines gave esters, thioesters, and amides of this same acid. The anhydride and chloride were obtained by further reactions. Some of the derivatives of fluorosulfonyldifluoroacetic acid and their physical properties are presented in Table 2.

The interaction of fluorosulfonyldifluoroacetic anhydride with antimony trichloride led to the formation of a compound identical to the original tetrafluoroethane-β-sultone. On the basis of this conversion cycle, of certain other properties of the addition product, and of the infrared spectra of the addition products and derivatives of the α-fluorosulfonylcarboxylic acids, it can be assumed that the products of the addition of sulfur trioxide (α-modification) to fluoroolefins are actually dynamic mixtures of pairs of isomers — the cyclic β-sultone and the linear difluoride of the sulfocarboxylic acid:

$$CF_2-CF_2-SO_2 \quad (O) \qquad F-C(=O)-CF_2-SO_2-F$$

TABLE 2

Prep. no.	Formula	B.p., °C	d_4^{20}	n_D^{20}	MR found	MR calc.
1	$F-SO_2-CF_2-COOH$	153	1,7234	1,3602	22,81	22,73
2	$(F-SO_2-CF_2-CO)_2O$	135—136	1,7441	1,3530	42,02	41,86
3	$F-SO_2-CF_2-CO-Cl$	67—68	1,6419	1,3570	26,15	26,14
4	$F-SO_2-CF_2-CO-OCH_3$	115	1,5159	1,3510	27,38	27,47
5	$F-SO_2-CF_2-CO-OC_2H_5$	129—130	1,3965	1,3565	31,60	32,08
6	$F-SO_2-CF_2-CO-OC_3H_7-i$	142—143	1,3478	1,3595	35,98	36,70
7	$F-SO_2-CF_2-CO-SCH_2CH_2Cl$	108—109*	1,5327	1,4533	45,33	43,11
8	$F-SO_2-CF_2-CO-NH-C_6H_5$	104—105**	—	—	—	—

* At 25 mm.

** Melting point.

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AN OXIDATION METHOD FOR THE SEPARATION OF SULFIDES FROM THE MIDDLE FRACTIONS OF PETROLEUM

E. N. Karaulova and G. D. Gal'pern

Institute of Petroleum, Academy of Sciences, USSR

(Presented by Academician A. V. Topchiev, July 29, 1958).

In an investigation of the irreversible oxidation potentials of organosulfur compounds, Luk'yanitsa and Gal'pern [1] found that the conversion sulfide → sulfoxide is clearly distinct from the oxidation of hydrocarbons and sulfur compounds of other groups. This provided a theoretical basis for the possible discovery of conditions for the selective oxidation of sulfides in petroleum distillate fractions to sulfoxides. We have recently selected such conditions [2]; it was shown that hydrogen peroxide in acetic acid can quantitatively oxidize sulfides to sulfoxides without touching the aromatic hydrocarbons and compounds of the thiophene series.• The method was

TABLE 1

Characteristics of the Concentrates Investigated

Concentrate no.	n_D^{20}	S_{tot}, %	Ssulfide		M	Yield, % orig. kerosene
			% of concentrate	% of S_{tot}		
I	1.5220	7.98	7.13	89.5	212	0.41
II	1.5425	2.07	0.94	30.6	173	1.90
III	1.5370	3.92	1.19	30.4	167	2.24
IV	1.5430	3.82	1.05	27.7	164	1.63
V	1.5300	8.18	4.46	54.8	169	0.78

developed using synthetic mixtures, and during this work, the formation of any other polar products except sulfoxides was not detected. A study of the adsorbability of sulfoxides [3] led to the conclusion that the separation of sulfoxides from aromatic hydrocarbons and thiophene compounds by adsorption chromatography is possible. Further development of the method for small scale separation of sulfoxides by selective oxidation and subsequent chromatographing was carried out on petroleum distillates. The distillates investigated were sulfur-aromatic concentrates from 175-300° fractions of Romashkin crude (the fractions comprised 17.2% of the crude). This crude is typical of Devonian crudes from the Ural – Volga Valley region.

The organosulfur compounds present in Romashkin petroleum have received absolutely no study. This lends an independent interest to the separation of sulfides, which constitute a substantial part of the organosulfur compounds in the middle cuts of Romashkin crude.••

• Mercaptans oxidize more easily than sulfides, forming the slightly polar disulfides; further oxidation of the disulfides to polar oxygenated derivatives takes place only after the oxidation of sulfides to sulfoxides.

•• The present work was reported at the 4th Scientific Session on the Chemistry of Sulfur and Nitrogen-containing Compounds in Petroleum and Petroleum Products, which was held in Ufa in July, 1958; it will be presented in detail in the Proceedings of the meeting, which are presently in press.

TABLE 2

Sulfoxides Obtained from Romashkin Petroleum

Compositions calculated from elemental analysis	x in the formula $C_nH_{2n-x}SO$	Empirical formula	Sulfoxide cont., % total sulfoxides separated from a given concentrate
	Concentrate I		
$C_{10,85}H_{19,80}SO_{1,38}$	2,90	$C_{11}H_{20}SO$	9,9
$C_{12,82}H_{22,77}SO_{1,03}$	2,27	$C_{13}H_{22}SO$	33,6
$C_{12,89}H_{24,09}SO_{1,18}$	1,69		
$C_{13,04}H_{24,50}SO_{1,25}$	1,66	$C_{14}H_{24}SO$	42,7
$C_{12,79}H_{23,00}SO_{1,11}$	1,68		
$C_{12,33}H_{23,30}SO_{1,33}$	1,48		
$C_{15,47}H_{28,48}SO_{1,23}$	2,48	$C_{15}H_{28}SO$	13,6
	Concentrate II		
$C_{14,42}H_{26,45}SO_{1,22}$	2,39	$C_{14}H_{26}SO$	65,3
$C_{14,72}H_{26,85}SO_{1,41}$	2,49		
$C_{15,45}H_{28,61}SO_{1,22}$	2,31	$C_{15}H_{28}SO$	32,4
$C_{15,53}H_{23,01}SO_{1,71}$	3,05		
	Concentrate III		
$C_{10,30}H_{18,45}SO_{0,88}$	3,15	$C_{11}H_{20}SO$	6,5
$C_{11,6}H_{20,6}SO_{1,0}$	2,6		
$C_{14,05}H_{26,49}SO_{1,22}$	1,61	$C_{14}H_{26}SO$	78,2
$C_{15,10}H_{28,21}SO_{1,06}$	1,99	$C_{15}H_{28}SO$	1,9
	Concentrate IV		
$C_{11,85}H_{20,33}SO_{0,97}$	3,17	$C_{12}H_{26}SO$	6,7
$C_{14,61}H_{26,75}SO_{1,07}$	2,47	$C_{14}H_{26}SO$	85,2
$C_{13,56}H_{26,19}SO_{1,21}$	0,93		
	Concentrate V		
$C_{10,13}H_{19,54}SO_{1,6}$	0,72	$C_{12}H_{26}SO$	39,4
$C_{12,32}H_{24,00}SO_{1,16}$	0,64	$C_{13}H_{24}SO$	17,0
$C_{12,54}H_{24,30}SO_{1,02}$	1,08		
$C_{12,97}H_{24,93}SO_{1,11}$	1,01	$C_{14}H_{26}SO$	43,5
$C_{13,03}H_{25,23}SO_{1,14}$	0,93		
$C_{13,67}H_{25,70}SO_{1,37}$	1,64		

The sulfur-aromatic concentrates were prepared by S. S. Nifontova, A. A. Suchkova and I. A. Musaev • by chromatographing the indicated kerosene fractions over ASM silica gel [4]. After separation of the total paraffinic and naphthenic hydrocarbons, the sulfur-aromatic portion was collected in individual fractions according to increasing refractive index; the resulting fractions were chromatographed repeatedly. The concentrates used in our investigations differed with respect to the highest sulfur content of each. They eluted from the chromatographic column following the fraction with $n^{20}D$ 1.53-1.54. It should be pointed out that their indices of refraction had a tendency to decrease with an increase in the total sulfur content (see Table 1).

The content of sulfide sulfur was determined for the concentrates investigated by potentiometric titration ([5] and the data of Gal'pern and co-authors). The concentrate charge (of the order of 200 g) was mixed with an

•Under the supervision of A. V. Topchiev in the S. S. Nametkin Laboratory of Petroleum Chemistry of the Institute of Petroleum, Academy of Sciences USSR.

TABLE 3

Fraction Balance After Oxidation and Chromatographing (calculated on the original concentrates)

Concentrate No.	Balance	
	% of S_{tot}	% of S sulfide
I	90.0	90
II	97.8	87
III	97	98.8
IV	95.8	98.7
V	95.7	96.7

equal amount of glacial acetic acid, and, with rapid stirring 27 percent hydrogen peroxide was added at 20-25°. After approximately 1 hour, 110% of the amount of H_2O_2 required for oxidation of the sulfides to sulfoxides was introduced. The mixture was stirred for another 2 hours and then poured into a three-fold amount of water. After 12 hours, the aqueous layer was separated, and the organic layer was washed with water. The aqueous extracts were concentrated (under the vacuum of a water aspirator), during which water was periodically added until the acetic acid was completely eliminated. The sulfoxides were extracted from the residue with ether. The organic layer was dried with calcium chloride and chromatographed over ASK silica gel (90-200 mesh, 225 g of silica gel per 100 g of adsorbate). The column was eluted with dearomatized petroleum ether with a boiling point not exceeding 65°, benzene, chloroform, and alcohol. The sulfoxides separated by the treatment described above are shown in Table 2.

The lightest sulfoxides, $C_{11}H_{22}SO$ and $C_{12}H_{26}SO$ from Concentrates I, III, and IV and $C_{10}H_{22}SO$ from Concentrate V, were separated from the aqueous layer.

The petroleum ether desorbate did not contain sulfoxides; the sulfur compounds in this fraction were not oxidized by H_2O_2 under our conditions. Only the $C_{15}H_{32}SO$ sulfoxides from Concentrate I were eluted by benzene. Chloroform eluted 40.5% of the $C_{11}H_{24}SO$ sulfoxides from Concentrate I and 72.3% of the $C_{11}H_{26}SO$ sulfoxides from Concentrate V. The remaining sulfoxides were eluted by alcohol. Judging from the composition of the sulfoxides, the original sulfides were completely saturated sulfur compounds. Only thiabicyclanes of the general formula $C_nH_{2n-2}S$ were present in the first three concentrates. In addition to thiabicyclanes, Concentrate IV contained a small amount of thiatricyclanes — $C_nH_{2n-4}S$. Only monocyclic sulfides of the general formula $C_nH_{2n}S$ were found in Concentrate V. The structure of these sulfoxides is a subject for further study.

The fraction balance prepared after oxidation and chromatographing (see Table 3) showed that our proposed method permits complete oxidation of the sulfides in the concentrates to sulfoxides practically without touching other groups of compounds and also the separation of the sulfoxides from aromatic hydrocarbons and unoxidized sulfur compounds.

The proposed method has a special significance for the manufacture of diesel fuels and other kerosene and light gas oil distillates, since a large part of the sulfur compounds in these petroleum products are sulfides and the hydrocarbon components are chiefly difficultly oxidizable compounds.

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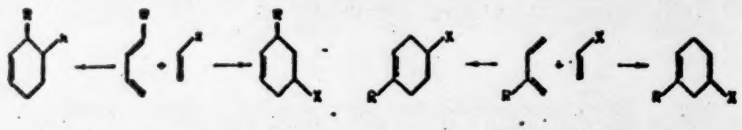
STRUCTURAL DIRECTIVITY OF DIENE CONDENSATIONS OF 1- AND 2-ALKYLBUTADIENES WITH UNSYMMETRICAL DIENOPHILES

Academician I. N. Nazarov, Iu. A. Titov and A. I. Kuznetsova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

The question of the effect of structural features on the course of the condensation of 1- and 2-alkylbutadienes with unsymmetrical dienophiles has attracted the attention of many investigators, since it may be assumed that such reactions will proceed in both possible directions with the formation of two structural isomers in each case:

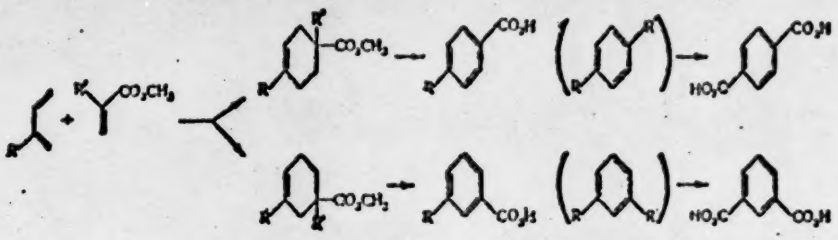


As has been shown by many workers in this field, when 2-alkyl-butadienes are condensed with unsymmetrical dienophiles, the chief product is the para isomer. However, from the mixture of addition products resulting from condensations of isoprene [1-9] and certain other 2-alkylbutadienes [6, 7, 10-12] with unsymmetrical dienophiles it has been possible to isolate significant amounts of the meta isomers also.

Reactions involving 1-alkylbutadienes proceed more selectively in a structural sense, and for a long time it was considered that only the ortho isomer is formed in condensation of this type. Only recently has it been possible to show the presence of a certain amount of the meta isomers among the addition products from the condensation of piperlyne [2, 5, 13] and 1-tertiarybutylbutadiene [12] with unsymmetrical dienophiles.

With the aim of investigating systematically the effect of the size of alkyl substituents in the diene and dienophile on the ratio of the resulting structural isomers, we studied the Diels-Alder condensation of esters of acrylic, methacrylic, and α-isopropylacrylic acids with isoprene, 2-propyl-, 2-isopropyl-, and 2-tertiarybutylbutadiene, piperlylene, and 1-isopropyl-, 1-butyl-, and 1-tertiarybutylbutadiene. All of the condensations were carried out under the usual conditions – by heating a mixture of the components in steel ampoules at 200° for several hours in the presence of 0.1-0.2% hydroquinone as a polymerization inhibitor. The method selected for the determination of the ratio of the structural isomers was the common method based on dehydrogenation of the mixture of addition products over 15-20% palladium on carbon at 340-350° and oxidation of the resulting alkylbenzoic acids or dialkylbenzenes with chromium trioxide or dilute nitric acid to a mixture of isomeric phthalic acids, which was resolved by crystallization of the barium salts. In some cases, the ratio of isomers could be established directly by fractional crystallization of the addition products.

In the case of the 2-alkylbutadienes, the composition of the resulting mixture of addition products was established according to the following scheme:



R = CH_3; C_2H_7; i-C_3H_7; tert -C_4H_9
R' = H; CH_3; i-C_3H_7

From the data presented above, it may be seen that the structural selectivity of the reaction increased with an increase in the size of the alkyl substituent in the 2-alkylbutadiene and dienophile, while the relative amount of the meta isomer in the mixture of addition products decreased sharply.

TABLE 1

Condensation of 2-Alkylbutadienes with Unsymmetrical Dienophiles

Diene (R)	Dienophile (R')	Yield of adduct, %	B. p.	Ref. Index	Ratio of para to meta isomer
CH_3	H	84 (2 hours)	88—90°/16 mm	n_D^{20} 1,4655	2:1
C_2H_7	H	81 (2 hours)	132—134°/30 mm	n_D^{20} 1,4650	2,4:1
i-C_3H_7	H	65 (5 hours)	106—109°/12 mm	n_D^{21} 1,4649	3:1
tert.-C_4H_9	H*	47 (5 hours)	109—112°/10 mm	n_D^{21} 1,4676	3,5:1
CH_3	CH_3	66 (2 hours)	92—94°/12 mm	n_D^{16} 1,4620	2,5:1
C_2H_7	CH_3	65 (2 hours)	133—135°/30 mm	n_D^{20} 1,4622	3,4:1
i-C_3H_7	CH_3	40 (5 hours)	106—110°/12 mm	n_D^{23} 1,4600	7,3:1
tert-C_4H_9	CH*	36 (5 hours)	110—112°/10 mm	n_D^{20} 1,4620	10:1
CH_3	i-C_3H_7**	43 (15 hours)	105—105°/10 mm	n_D^{20} 1,4676	4,2:1
i-C_3H_7	i-C_3H_7**	31 (10 hours)	110—114°/10 mm	n_D^{17} 1,4703***	14:1
tert-C_4H_9	i-C_3H_7*,**	15 (10 hours)	123—126°/10 mm	n_D^{20} 1,4275***	only para

* The ratio of isomers was established directly by crystallization of the addition products (after saponification).

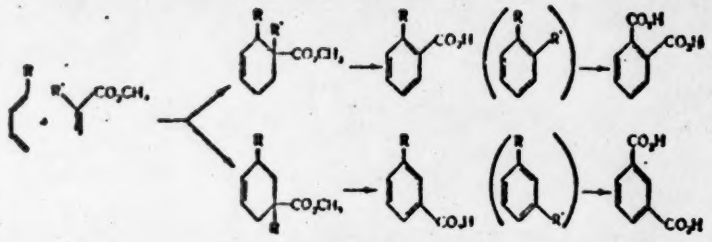
** Condensations carried out with the ethyl esters.

*** The products contained dimers of the original diene which could not be separated by distillation.

The opposite rule held for the formation of structural isomers in the case of 1-alkylbutadienes, for which the system used to determine the ratio of isomers and the results obtained are presented below.

As may be seen from Table 2, in the case of 1-alkylbutadienes, the relative amount of the meta isomer in the resulting mixture of addition products appreciably increased with an increase in the size of the alkyl substituent in the diene and dienophile.

Such a difference in the ratio of the structural isomers for 1- and 2-alkylbutadienes cannot be explained only by changes in the electronic effects of the alkyl groups, since if such were the case, the ratio of isomers would change in the same direction in both series of dienes.



R = CH_3; i-C_3H_7; C_4H_9; tert-C_4H_9
R' = H, CH_3; i-C_3H_7

TABLE 2

Condensation of 1-Alkylbutadienes with Unsymmetrical Dienophiles

Diene (R)	Dienophile (R')	Yield of adduct, %	Constants of adducts		Ratio of ortho to meta isomer
			B. p.	ref. index n_D^{20}	
CH_3	H	85 (2 hours)	94—97 °/30 mm	1,4580	6,8:2
i-C_3H_7	H	60 (5 hours)	99—101°/10 mm	1,4633	5:1
C_4H_9	H	74 (5 hours)	143—146°/40 mm	1,4660	5,1:1
tert.-C_4H_9	H	76 (5 hours)	122—125°/20 mm	1,4665	4,1:1
CH_3	CH_3	68 (2 hours)	88— 91°/15 mm	1,4631	4,9:1
i-C_3H_7	CH_3	52 (2 hours)	113—117°/20 mm	1,4642	3,1:1
tert.-C_4H_9	CH_3	75 (2 hours)	132—135°/25 mm	1,4735	2,6:1
CH_3	i-C_3H_7*	33 (15hours)	102—105°/8 mm	1,4670	2,5:1
i-C_3H_7	i-C_3H_7*	32 (10hours)	118—124°/10 mm	1,4682**	2,4:1
tert.-C_4H_9	i-C_3H_7*	19 (10hours)	135—140°/25 mm	1,4680**	0,9:1

* Condensations carried out with ethyl esters.

** The products contained some of the original diene, which could not be separated by distillation.

These results apparently can be explained by the considerable effect of steric factors, since with an increase in the steric hindrance caused by an increase in the size of the substituents, there can be an increase in the fraction of only those isomers (meta isomers for 1-substituted and para isomers for 2-substituted dienes) whose formation proceeds through the less sterically hindered transition complex.

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AN INTERESTING CASE OF ISOMERIZATION AMONG THE SATURATED ALIPHATIC NITRO COMPOUNDS

S. S. Novikov, A. A. Fainzel'berg, S. A. Shevelev, I. S. Korsakova and K. K. Babievskii

N. D. Zelinksii Institute of Organic Chemistry, Academy of Sciences, USSR

(Presented by Academician A. V. Topchiev, July 14, 1958)

During the study of the chemical properties of the recently prepared 1,1,1,3-tetranitropropane [1] we found that this polynitroalkane converts to the isomeric symmetrical tetranitropropane in the presence of ammonia (it separates from the reaction mixture in the form of the diammonium salt):

$$(NO_2)_3CCH_2CH_2NO_2 \xrightarrow{NH_4OH} \underset{\displaystyle NH_4O_2N \quad NO_2NH_4}{NO_2CCH_2CNO_2}$$

Along with the symmetrical tetranitropropane, some 1,1,3-trinitropropane is formed:

$$(NO_2)_3CCH_2CH_2NO_2 \xrightarrow{NH_4OH} \underset{\displaystyle NO_2NH_4}{NO_2CCH_2CH_2NO_2}$$

Symmetrical tetranitropropane is not formed when stronger organic or inorganic bases are substituted for the ammonia, and the sole reaction product is 1,1,3-trinitropropane. Thus, the action of dimethylamine on 1,1,1,3-tetranitropropane results in a 73-74% yield of 1,1,3-trinitropropane.

The formation of 1,1,3-trinitropropane is explained by the elimination of a nitro group from the trinitromethyl group of the 1,1,1,3-tetranitropropane under the influence of basic media. In the presence of ammonia, this process proceeds concurrently with the isomerization of 1,1,1,3-tetranitropropane to symmetrical tetranitropropane and is competitive with this reaction. In the presence of bases stronger than ammonia, the isomerization reaction is practically completely suppressed, and only the elimination of a nitro group from the 1,1,1,3-tetranitropropane occurs.

The optimum conditions for the isomerization of 1,1,1,3-tetranitropropane to symmetrical tetranitropropane are a temperature of 0°, a reaction time of 1-2 hours, and an aqueous-alcoholic medium (the reaction does not go in nonpolar solvents). Under these conditions, the yield of the diammonium salt of symmetrical tetranitropropane is 40%; in addition, some of the ammonium salt of 1,1,3-trinitropropane is formed. This ammonium salt can be converted to the potassium derivative by the action of potassium chloride. The action of bromine on the dipotassium salt of symmetrical tetranitropropane gave the corresponding dibromide – 1,3-dibromo-1,1,3,3-tetranitropropane. All of the compounds prepared in the present work are described here for the first time. It should be pointed out that the conversion of 1,1,1,3-tetranitropropane to symmetrical tetranitropropane is the first case of isomerization by a nitro group shift among the saturated aliphatic nitro compounds. We are presently studying the mechanism of this interesting reaction.

EXPERIMENTAL

The original 1,1,1,3-tetranitropropane was prepared by the addition of nitroform [trinitromethane] to nitroethylene [1].

Isomerization of 1,1,1,3-tetranitropropane to 1,1,3,3-tetranitropropane under the influence of ammonia. 1.5 ml (0.02 mole) of 30% aqueous ammonia was added over a period of 20 minutes, with stirring, to a solution of 2.24 g (0.01 mole) of 1,1,1,3-tetranitropropane in 20 ml of alcohol; during the addition, the temperature was maintained at 2-4° (ice cooling); after the addition of the ammonia was complete, the mixture was stirred for 2.5 hours at 0°, and the resulting yellow precipitate, the diammonium salt of 1,1,3,3-tetranitropropane, was carefully suction filtered (the filtrate was retained for further work). The yield was 1.05 g (40%). This salt was dissolved in a mixture of 10 ml of alcohol and 20 ml of water, 2 g of potassium chloride was added, and the mixture was stirred for another 15-20 minutes and then cooled with ice; the resulting yellow crystalline precipitate of dipotassium salt of 1,1,3,3-tetranitropropane was filtered, washed with a small amount of ice water and then twice with small portions of acetone and ether, and dried in air. The yield was 1 g (33.3%). The salt was recrystallized from water at 50-60°. The decomposition temperature of the recrystallized sample was 225° (with very rapid heating).

Found %: K 25.72; 25.72; C 11.86; 12.18; H 0.91; 0.97; N 18.63; 18.61 $C_3H_2N_4O_8K_2$. Calculated %: K 26.03; C 11.99; H 0.67; N 18.66

An increase or decrease in the temperature decreased the yield of symmetrical tetranitropropane; an increase in the reaction time and also in the amount of ammonia had no effect on the yield.

To the alcoholic filtrate remaining after separation of the diammonium salt from the reaction mixture was added 20 ml of water, during which time the solution was cooled with ice, 2 g of potassium chloride was then added with stirring, and the stirring was continued for another 15-20 minutes; the yellow precipitate, the monopotassium salt of 1,1,3-trinitropropane, was suction filtered, washed with small amounts of ice water, alcohol, and ether, and dried in air. The yield was 0.15 g (6.9%). The decomposition temperature of the salt, after recrystallization from water, was 211-213° (with a heating rate of 5° per minute).

Found %: K 18.33; 17.99; N 19.65; 19.84 $C_3H_4N_3O_6K$. Calculated %: K 18.00; N 19.35

The free 1,1,3,3-tetranitropropane can be obtained from the dipotassium salt by the action of sulfuric acid: to a mixture of 3 g (0 01 mole) of the pure dipotassium salt of 1,1,3,3-tetranitropropane, 20 ml of water, and 40 ml of ether was added, with stirring, 9 ml of cold 20% sulfuric acid, the temperature being maintained at 0° by means of ice. The ether layer was separated and dried with calcined magnesium sulfate. Evaporation of the ether gave 1.9 g (85%) of a yellow oil, 1,1,3,3-tetranitropropane. This compound, in contrast to 1,1,1,3-tetranitropropane, decomposed on standing in air. On interaction with ammonia in dry ether solution, the 1,1,3,3-tetranitropropane was smoothly converted to the expected diammonium salt, which could be converted to the dipotassium salt by the action of potassium chloride.

Preparation of 1,3-dibromo-1,1,3,3-tetranitropropane. 12 g (0.004 mole) of the dipotassium salt of 1,1,3,3-tetranitropropane was covered with 12.5 ml of dry ether, and 1.3 g (0.008 mole) of bromine was gradually added while the reaction mixture was stirred and cooled with ice. The reaction mixture was then stirred for an hour at room temperature, the ether solution was separated, the precipitate (potassium bromide) was washed with ether, and the combined ether solutions were dried over calcium chloride; the ether was then evaporated to leave a residue of 1,3-dibromo-1,1,3,3-tetranitropropane. The yield was quantitative; the m.p. was 69-69.5° (from CCl_4).

Found %: Br 41.52; 41.44; $C_3H_2N_4O_8Br_2$. Calculated %: Br 41.34

Conversion of 1,1,1,3-tetranitropropane to 1,1,3-trinitropropane in the presence of dimethylamine. To a solution of 2.24 g (0.01 mole) of 1,1,1,3-tetranitropropane in 15 ml of alcohol was added, with stirring, 3 ml (0.02 mole) of a 33% aqueous solution of dimethylamine while the solution was maintained at a temperature of 0° by cooling with ice. After the addition of the dimethylamine, the mixture was stirred for another 30 minutes at 0° and then for 1 hour at 10°. 15 ml of water and then 2 g of potassium chloride were added, with stirring, to the resulting dark brown solution, the mixture was stirred for another 15 minutes, cooled to 5°, and the crystalline monopotassium salt of 1,1,3-trinitropropane was filtered, washed with small amounts of ice water, alcohol, and ether, and dried in air. The yield was 1.6 g (73.7%).

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SYNTHESIS OF DERIVATIVES OF CYCLIC β-DIKETONES

V. V. Perekalin and K. S. Parfenova

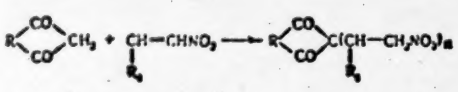
(Presented by Academician M. I. Kabachnik, August 23, 1958)

As an amplification of our investigations in the field of unsaturated nitro compounds, we studied their reaction with certain cyclic β-diketones.

The aim of this work was to accomplish the synthesis of different cyclic β-diketones substituted at an active methylene group.

Interest in the present investigation was heightened by the increased pharmacological values of cyclic β-diketones, which have found widespread use as blood anticoagulants (phenyl-1,3-indanedione). Indications of their antispasmodic and atropine-like action are well known.

The condensation of various cyclic diketones (dimedone, 1,3-indanedione, and 2-phenyl-1,3-indanedione) and the related 4-hydroxycoumarin with a series of aliphatic, aromatic, and heterocyclic unsaturated nitro compounds was accomplished in the presence of basic catalysts (sodium methylate, triethylamine) in organic solvents (methanol, benzene) at room temperature.



R_1 = H, alkyl, aryl, heterocyclic; n = 1,2. R = (CH)

With dimedone, only nitroethylene reacted in a ratio of 2 moles per mole of diketone (without a catalyst); the aromatic nitroolefins formed monomolecular addition products. However, 1,3-indanedione reacted both of the hydrogen atoms of its methylene group with all of the nitroolefins tested (nitroethylene, β-nitrostyrene, furylnitroethylene, and thienylnitroethylene). 4-Hydroxycoumarin could be condensed only with β-nitrostyrene; the the aliphatic nitroolefins (nitroethylene) polymerized under the conditions of the reaction, while aromatic nitroolefins containing a nucleophilic substituent on the benzene ring (4-dimethylamino and 4-methoxy groups) did not react owing to the decreased activity.

TABLE 1

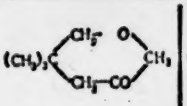
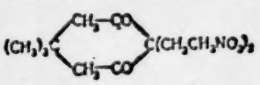
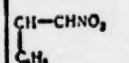
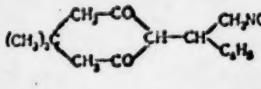
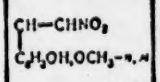
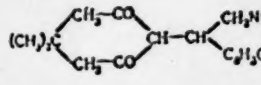
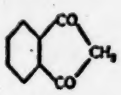
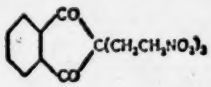
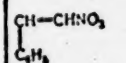
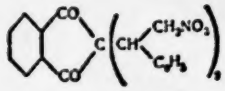
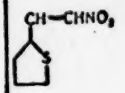
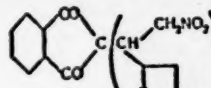
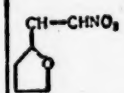
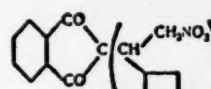
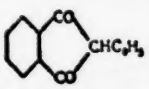
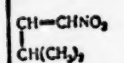
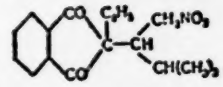
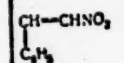
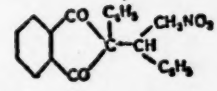
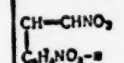
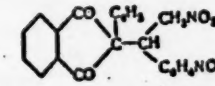
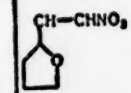
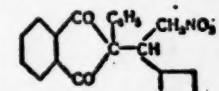
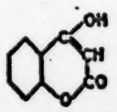
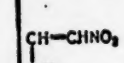
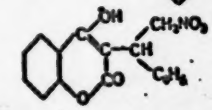
Reaction product	Yield, in percent*	
	benzene	methanol
(V)	76	45
(VII)	54	23
(VIII)	83	Reaction did not go
(IX)	59	45
(XI)	55	41.5

* Reaction time 1 hour.

The formulas of the substances synthesized, the reaction conditions, and the results of the analyses are presented in Tables 2 and 3.

The components containing the methylene group can be arranged in approximately the following series with respect to decreasing activity in the reaction: 2-phenyl-1,3-indanedione, 1,3-indanedione, dimedone, 4-hydroxycoumarin.

TABLE 2

Starting materials		Final product*	Reaction time, hours	Yield, %
methylene component	nitroolefin			
	$CH_2=CHNO_2$	(I) 	0,5	52
		(II) 	3	65
		(III) 	72	47
	$CH_2=CHNO_2$	(IV) 	1,5	35
		(V) 	3	85
		(VI) 	3	80,6
		(VII) 	3	54
		(VIII) 	10	83
		(IX) 	10	82,3
		(X) 	10	87
		(XI) 	1	55
		(XII) 	24	50

* Products (I)-(III) and (XII) were prepared in a methanol medium in the presence of sodium methylate; products (IV)-(XI) were prepared in benzene in the presence of triethylamine.

TABLE 3

Substance	M.p., °C	Found, %			Calculated, %		
		C	H	N	C	H	N
(I)	99—100	50,38 50,40	6,58 6,34	9,90 9,98	50,34	6,29	9,79
(II)	135	66,27 66,32	6,78 6,79	4,97 4,83	66,35	6,56	4,80
(III)	178—179	61,68 61,19	6,72 6,78	4,67 4,89	61,47	6,83	4,17
(IV)	110	53,15 53,15	4,36 4,31	9,70	53,4	4,11	9,58
(V)	194	67,81 67,59	4,76 4,61	6,14 6,13	67,5	4,5	6,3
(VI)	213	54,98 55,23	3,28 3,45	5,95 5,80	55,26	3,5	6,13
(VII)	156			6,50 6,81			6,60
(VIII)	136—137	71,16 71,15	5,91 5,88	4,34 4,03	71,21	5,63	4,15
(IX)	165	74,13 74,30	4,68 4,72	4,15 4,04	74,36	4,34	3,75
(X)	193	66,14 66,31	3,71 3,92	7,10 7,45	66,34	3,84	6,97
(XI)	132	69,98 69,92	4,43 4,17	3,90 4,06	69,79	4,15	3,87
(XII)	155—157	65,15 65,25	4,86 4,51	4,66 4,54	65,29	4,18	4,50

Strongly acid diketones ($K_{DIS} \approx 10^{-1}$) – 2-nitrodimedone, 2-nitro-1,3-indanedione, and 1,3-indanedione-2-sulfonic acid – did not react with nitroolefins. Apparently only β-diketones having optimum acidity, which determines the lability of the hydrogen atoms of the methylene group, are capable of condensing with nitroolefins.

The reaction medium has a substantial effect on the success of the reaction.

Nonpolar solvents (benzene) do not promote enolization of cyclic β-diketones [1], which undergo Michael condensation in the keto form [2], and therefore such solvents favor the reaction; polar solvents (methanol) have the opposite effect.

The nitro derivatives resulting from the syntheses were converted to the corresponding amines by catalytic hydrogenation over nickel catalyst.

This proposed method for the synthesis of derivatives of cyclic β-diketones consists of replacement of the hydrogen atoms of the methylene group of the diketone by a nitroethyl group connected to different alkyl, aryl, and heterocyclic groups.

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PREPARATION OF CRYSTALLINE TRANS-1,4-POLYBUTADIENE AND TRANS-1,4-POLYISOPRENE AND A STUDY OF THEIR PROPERTIES

E. I. Tinyakova, Corresponding Member AN SSSR B. A. Dolgoplosk, A. I. Marei and M. Z. Al'tshuler

Institute of High-molecular Compounds, Academy of Sciences, USSR
S. V. Lebedev All-Union Scientific Research Institute of Synthetic Rubber

Crystalline diene polymers (trans-1,4- and cis-1,4-polybutadienes and polyisoprenes) having an ordered structure were first prepared by Natta and co-workers who used catalysts formed by the interaction of organoaluminum compounds with halides of metals having variable valence [1].

We have found that ordered trans-1,4-polymers of butadiene and isoprene can be prepared using oxide catalysts, in particular, chromium oxide on silica-alumina. In the present communication, we present the first results of our work in this field.

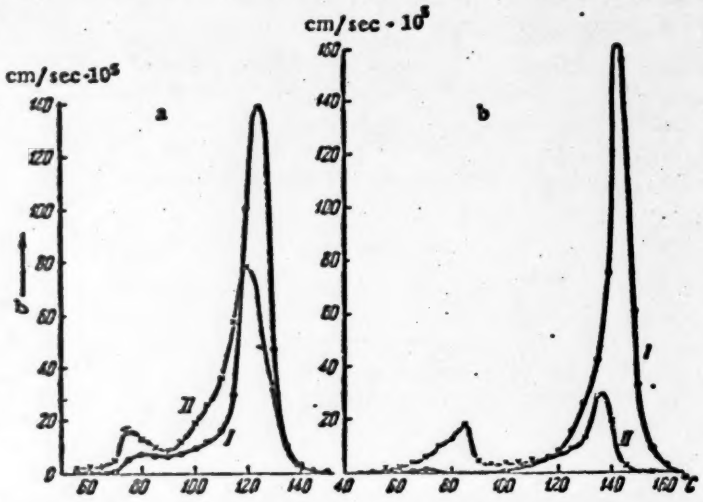

Fig. 1. Differential curves showing the relationship between the rate of deformation of polybutadiene and temperature. I and II indicate the cycles. Heating in Cycle I was to 220° for Graph a and to 250° in the case Graph b.

The catalyst was prepared by impregnating silica-alumina (10% Al_2O_3 and 90% SiO_2) with a solution of chromium trioxide and subsequent activation with dry air (5 hours at 500-550°). The polymerization was carried out at 79-80° in solution in benzine (bp. 100-130°) or toluene, which were used in a ratio of 2 volumes per volume of

monomer. The components were charged to ampoules under an atmosphere of dry, oxygen-free nitrogen. The isoprene polymer was separated from the catalyst by solution in hot benzene, while the butadiene polymer was separated by solution in hot xylene. The hot polymer solution was filtered from catalyst, excess solvent was distilled under vacuum, and the polymer was precipitated with methyl alcohol and dried under vacuum to constant weight. In order to protect the polymer from oxidation at all stages of the separation, phenyl-β-naphthylamine or aldol-α-naphthylamine was introduced into the solution. In all cases, polymerization was practically complete after 10-12 hours; the yield of polymer was quantitative.

TABLE

Change in Density of Polybutadiene During Heating

Test cycle	Max. temp. during test, °C	Heating time at max. temp., hr	Polymer density		Polymer solubility in hot toluene, %	
			sample no. 1	sample no. 2		
Original sample	—	—	1,015	0,970	100	Sample no. 1
I	220	—	1,006	0,968	47	
II	230	2	0,988	—	33	
	270	2	—	0,923	—	Sample no. 2
III	270	3	—	0,913	0	
IV	290	1,5	—	0,966	0	
V	300	4,5	—	0,999	0	

Polyisoprene. The polyisoprene was a solid product which began to soften at a temperature of 38-40°. According to infrared data*, 99% of the units of the polymer chain had trans-1,4-configuration, and 1% of the units had added by 3,4-addition. Thus, this polyisoprene was practically pure trans-1,4-polymer. Its unsaturation, as determined by reaction with iodine monochloride [2], was 100% of that required by theory (iodine number 370-374). In conformity with its high ordered structure, the polymer was crystalline, a fact which was confirmed by x-ray data (Figure 2 a). X-ray patterns obtained for the polyisoprene and for natural β-gutta-percha were similar.

Polybutadiene. Our polybutadiene was a crystalline, fibrous substance, insoluble in benzine and benzene at ordinary temperatures and readily soluble in hot toluene. In connection with this, an investigation of the absorption spectrum of the polybutadiene in the infrared region was carried out on films prepared by extrusion at a temperature of 130° and 150 atm. The resulting spectrum had a sharp maximum in the region corresponding to a trans-1,4-configuration of the polymer units. There was practically no absorption in regions corresponding to 1,2- and cis-1,4-units.

X-ray patterns of unstretched polybutadiene films are shown in Figure 2 b.

This polymer was characterized by a high density. Different samples of polybutadiene prepared in solution in benzene had densities of 0.991 to 1.015 as against 0.92 for amorphous polymer; the density of the first fraction which separated as the polymer was washed from the catalyst surface was somewhat lower than the succeeding fraction. This was especially noticeable for polymers prepared by polymerization in toluene solution (the density of the last fractions was 1.010-1.005, while the density of the first fractions was 0.98). The decreased density of the first fractions and their better solubility is connected with the presence of disturbances in the structure of the chain.

We also studied the temperature dependence of deformation rate of the polybutadiene under a constant compressive load (25 kg/cm²). The work was carried out with a modification of the apparatus used for the determination of the glass temperature of rubbers [3]; this permitted heating the samples to 400°. The temperature was increased at a rate of 2-3°/minute. The testing was carried out with samples in the form of cylinders 6-7 mm high and 7 mm in diameter, which were prepared by extruding the polymer at a temperature of 130-150° and a pressure of 100 atm.

* The infrared spectrum of polyisoprene was obtained by K. V. Nel'son, and that for polybutadiene was obtained by E. I. Pokrovskii; the x-ray patterns were taken by L. A. Volkova.

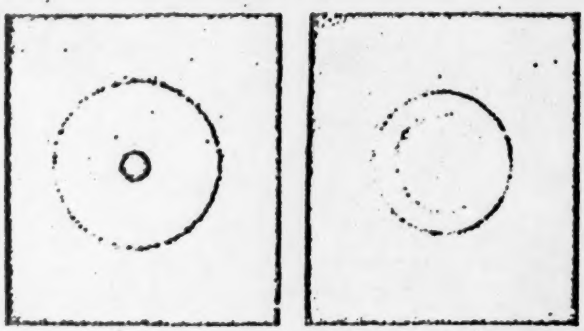

Fig. 2. x-Ray photographs of polyisoprene (a) and polybutadiene (b).

After taking a deformation–temperature curve (Cycle I), the sample was cooled to room temperature and the same relationship was determined a second time (Cycle II). Cycle III of the test was carried out on the same sample. In certain cases, the sample was brought to a predetermined temperature and held there for several hours. The course of the curves was readily reproducible with different samples. In Figure 1 are presented typical differential curves illustrating the rate of deformation at different temperatures.

The curves are characterized by the presence of two maxima. The first, small maximum, which corresponds to a temperature of 75-80°, is apparently due to defective crystals which melt at a lower temperature. The height of the first maximum increased in Cycles II and III. A certain decrease in the density of the polymer (see Table) corresponds to this increase in height of the maximum. The second, major maximum occurred at a temperature of 125-140°, which is apparently also the melting point of trans-1,4-polybutadiene. The sharp decrease in the yield of the polymer to compression at temperatures above the melting point (above 140°) is due to partial cross-linking of the polymer. Secondary processes of cross-linking of polymers in the crystalline state at elevated temperatures close to the crystalline melting point apparently proceed more intensively than in amorphous polymers under the same conditions. This effect is analogous in its nature to the effect of high pressures on the rate of chemical reactions, particularly polymerization processes. The height of the second maximum decreases from Cycle I to Cycle III, and the decrease is more, the higher the temperature and the longer the time the sample is heated. At the same time, there is a loss of solubility of the polymer and a decrease in its density, which, in some cases, drops to the density of an amorphous polymer (see Table).

At higher temperatures (270° and above), after the period of decreasing polymer density corresponding to the transition to the amorphous state, there was a period of increasing density. The latter period was due to considerable development of the process of cross-linking owing to the double bonds in the polymer chain.

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SELECTIVE HYDROGENATION OF THE ACETYLENIC BOND IN 2-BUTYNE-1,4-DIOL TO AN ETHYLENIC BOND OVER NICKEL CATALYST

L. Kh. Freidlin, Academician A. A. Balandin and I. F. Zhukova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

2-Butene-1,4-diol had found application in various syntheses, and its preparation by selective hydrogenation of commercially available 2-butyne-1,4-diol has served as a subject for a number of investigations. Pt catalyst with the addition of a small amount of sodium acid phosphate, boric acid, or piperidine and Co catalyst poisoned with 0.1% potassiumthiocyanate have been recommended for the selective hydrogenation of butynediol to butenediol. The conditions used with these catalysts were not given. It is also possible to use iron carbonyl, the reaction being carried out at 50° under a hydrogen pressure of 200 atm. [1]. Selective hydrogenation to butenediol cannot be carried out over nickel–copper or skeletal nickel catalysts [2], which are used for the hydrogenation of butynediol to butanediol. Reference [3] also indicates that the reaction is not selective when carried out in ethyl alcohol over skeletal nickel catalyst. After absorption of 1 mole of hydrogen, butanediol (11%) and certain other products of side reactions are found in addition to butenediol (66%) [3]. Nazarov, Bergel'son and co-workers [4] found that when the reaction is carried out in methyl alcohol with $Pd/CaCO_3$ catalyst, the reaction rate drops sharply after the absorption of 1 mole of hydrogen, and they therefore concluded that the process is stepwise. Judging from the fractionation results, by-products (10-20%) are also formed in the presence of Pd catalyst.

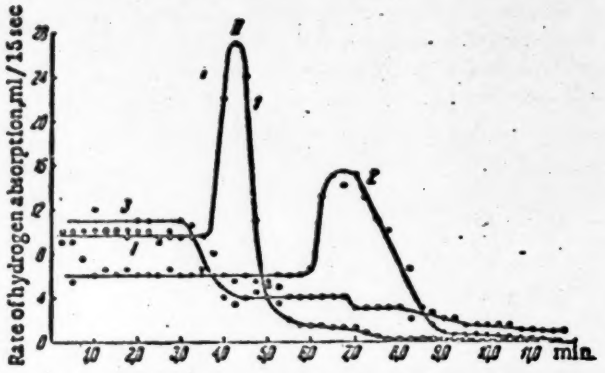

Fig. 1. Hydrogenation of butynediol in methyl alcohol (1), dioxane (2), and dimethylformamide (3).

It is well known that acetylenic hydrocarbons are usually selectively hydrogenated to ethylenic hydrocarbons over skeletal nickel catalyst in the presence of pyridine (or quinoline) [5].

It seemed of interest to determine whether selective hydrogenation of butynediol is possible under these conditions. Two series of experiments were carried out. One series was at normal pressure, 20°, and with vigorous

TABLE

Expt. no.	Taken for the reaction			H consumption			Av. rate of hydrogen absorption, ml/15 min		Half-life of reaction
	butynediol, g	pyridine, ml	solvent*, ml	theor., ml**	in portion I of kinetic curve		1st mole	2nd mole	
					ml	mol.			
1	0,5106	0	13, e. a.	133	248	1,87	11,0	26,0***	3,5
2	0,5006	0	6, m. a.	130	233	1,79	10,0	27,0***	3,7
3	0,5006	0	10, diox.	130	238	1,78	6,0	13,0***	6,0
4	0,5088	0	13,dmf.	133	238	1,79	10,2	1,0	4,0
5	0,5095	0,5	13, e.a.	133	133	1,00	9,5	0,3	4,2
6	0,5095	0,5	13, e.a.	133	133	1,00	9,4	0,3	4,0
7	0,5114	1,0	13, e.a.	133	133	1,00	10,6	0,3	3,5
8	0,5006	0,5	6, m.a.	130	130	1,00	7,2	0,3	5,2
9	0,5006	5,0	6, m.a.	130	130	1,00	—	0,0	12,0
10	2,6149	5,0	6, m.a.	693	741	1,06	—	0,0	175
11	0,5075	5,0	pyr.	132	142	1,08	—	0,0	12,0
12	2,2629	5,0	pyr.	590	630	1,06	—	0,2	109
13****	0,5083	0	25, e.a.	133	234	1,76	5,0	13***	7,2
14****	0,5114	1,0	25, e.a.	133	137	1,03	—	0,0	11,7
15****	0,5006	0,5	6, m.a.	130	133	1,02	—	0,0	19,5

* E.a. – ethyl alcohol; m.a. – methyl alcohol; diox. – dioxane; dmf. – dimethylformamide; pyr. – pyridine.

** Calculated for half the total possible hydrogenation.

*** Maximum rate.

**** In the presence of butanediol.

agitation 350 complete oscillations of the rocker per minute); the second series was also at 20°, but was in a rotating autoclave under pressure. The catalyst preparation and the experimental method have been described previously [5]. Each portion of catalyst (0.29 g) was used once. The experimental conditions and results are presented in Table 1. Figure 1 shows the variation in the rate of hydrogen absorption with time. The rate of the process was characterized by the half-life of the reaction and by the rate of absorption of hydrogen along the horizontal portions of the curves and at the maxima. It may be seen from Table 1 and Figure 1 that butynediol was hydrogenated to butenediol when the reaction was carried out in solution in ethyl or methyl alcohol; 1.79-1.87 moles of hydrogen was absorbed (Experiments 1 and 2). The first mole of hydrogen was absorbed at constant rate (Portion I), after which the reaction rate rose sharply (Portion II). This indicates the stepwise nature of the process over nickel, and it confirms that successive hydrogenation of the C≡C- and C=C- bonds does not depend on

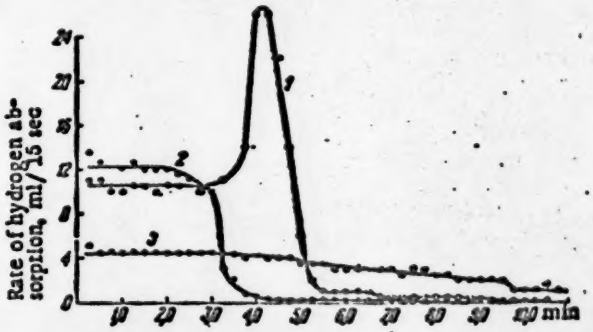

Fig. 2. Hydrogenation of butynediol in ethyl alcohol (1), ethyl alcohol + 0.5 ml pyridine (2), and pyridine (3).

the rates of these reactions. The curve for the addition of hydrogen to butynediol in dioxane has the same form as the curve for the reaction in alcohol, but the rate in both stages of the process is about half that in alcohol (Experiment No. 3). In contrast to the reactions in alcohol and dioxane, in a medium of dimethylformamide the second mole of hydrogen is absorbed at a considerably lower, rather than higher rate than the first mole (Experiment No. 4).

Successive experiments were carried out in alcoholic solution in the presence of pyridine. The catalyst was washed with alochol, presaturated with hydrogen, and agitated with a mixture of alcohol and pyridine; a weighed amount of butynediol in alcohol was then introduced, and hydrogenation was begun. It was found when low concentrations of pyridine were used (4-8%), the successive hydrogenation of the C≡C- and C=C- bonds was again readily fixed kinetically, though the maximum on the hydrogen absorption curve disappeared. It can be seen from Experiments 5-7 and Figure 2 that in the presence of 0.5-1 ml of pyridine, the rate of absorption of the first mole of hydrogen was no lower, while that of the second mole was considerably lower.

In experiments with an increased concentration of pyridine in methanol (Experiments 9 and 10) and with pyridine alone (Experiments 11 and 12), the hydrogenation curves were generally descending (Figure 2); after the absorption of one mole of hydrogen, the reaction stopped, thereby demonstrating the selective action of the catalyst. The sharply distinct effect of the treatment of the catalyst with small portions of pyridine on the rates of absorption of the first and second moles of hydrogen also shows that butynediol hydrogenates in two successive stages over nickel catalyst. Small amounts of pyridine have no effect on the rate of addition of hydrogen to the acetylenic bond, but they strongly inhibit the hydrogenation of the ethylenic bond. An analogous selective action was observed in the presence of piperidine and quinoline.

The components taking part in the process can apparently be arranged in the following order of decreasing adsorption on nickel catalyst: butynediol > pyridine > butenediol. Adsorption equilibrium is reached rapidly, since an increase in the time of the preliminary treatment of the catalyst with pyridine from 10 minutes (Experiment 5) to 20 minutes (Experiment 6) to 1 hour (Experiment 7) had no effect on the rate of absorption of the second mole of hydrogen. Butenediol can also be adsorptively displaced by butanediol, since in Experiments 14 and 15 with low concentrations of pyridine in alcohol and in the presence of butanediol (0.51 g), only 1 mole of hydrogen was absorbed. In Experiments 5-8, under similar conditions but with no butanediol present, absorption of a second mole of hydrogen occurred, although at a low rate.

As seen from Table 1, with an increase in the concentration of pyridine in alcohol (Experiments 9 and 10) and also in pyridine alone (Experiments 11 and 12), hydrogenation of the acetylenic bond to ethylenic proceeds very slowly. With the aim of accelerating the process, an experiment was carried out under 15 atm. of hydrogen. As was expected, the reaction under hydrogen pressure in the presence of pyridine proceeded selectively and considerably faster.

Catalyzates from experiments in which increased amounts of butynediol were used and which were carried out both at normal and elevated pressures were distilled under vacuum. After distillation of the solvent at 110-111° and 6.5 mm, butenediol with $n^{21}D$ 1.4770–1.4778 distilled. Literature data for butenediol: b.p. 135°/13 mm; $n^{20}D$ 1.4780 [3, 4]. 0.53 g of this butenediol was hydrogenated over skeletal nickel at 20°. The consumption of hydrogen corresponded to that theoretically required.

The results of our work show that during the hydrogenation of 2-butyne-1,4-diol over skeletal nickel catalyst in alcohol or dioxane, the second mole of hydrogen is absorbed at a considerably higher rate than the first. Small amounts of pyridine had no effect on the reaction rate in the first stage and sharply decreased it in the second stage. The half-hydrogenated product in the presence of pyridine is butenediol. Our data indicate a stepwise nature for the hydrogenation of butynediol and that skeletal nickel acts selectively in the presence of pyridine, both at normal and at elevated hydrogen pressure.

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CRYSTALLINE MIXED ORGANOZINC COMPOUNDS

N. I. Sheverdina, L. V. Abramova and Corresponding Member AN SSSR K. A. Kocheshkov

L. Ya. Karpov Physicochemical Scientific Research Institute

Zinc compounds having the formual R_2Zn (where R is alkyl) have been known in the pure state for more than a hundred years [1]; however, in spite of the considerable length of time since this investigation, mixed organozinc compounds of the type RZnX have not yet been isolated in the crystalline state, although numerous syntheses have been sucessfully carried out with their solutions [2].

It is a remarkable fact that the many investigators dealing with solid organozinc compounds as intermediate stages in the preparation of dialkylzincs did not characterize these compounds by isolating them in the pure form and analyzing them; consequently, their composition was not proved.

In 1903, Gvozdov [3], having available a crystalline compound obtained from ethyl iodide and zinc, made an attempt to crystallize it from ethyl iodide as a solvent, but he neither analyzed the substance nor ascribed to it any specific formula. Blaise [2], by the action of zinc bromide on an arylmagnesium bromide obtained a complex compound which had two metal atoms – zinc and magnesium – in the molecule. Finally, Garrett and coworkers [4] recently investigated the system diethylzinc-zinc bromide in hexane, but without isolating any compound.

In our systematic studies of the problem of individual crystalline organometallic compounds of the first to third groups of the periodic system and complexes of these compounds, we undertook the problem of isolating mixed organozinc compounds of the aliphatic and aromatic series in the form of complexes with ether or dioxane and of determining their composition.

It seemed to us that there are three basic synthesis routes to such compounds: 1) the direct action of zinc on alkyl halides, 2) the action of zinc halides on organomagnesium compounds, and 3) disproportionation through the action of zinc halides on dialkylzincs or diarylzincs.

As is well known, the first route is applicable only to aliphatic halogen derivatives, and actually only to iodides. (The reaction of metallic zinc with a mixture of alkyl bromides and iodides by Noller's method [5] is inapplicable, since it can lead to a mixture of RZnX with different halides.)

The second route (Blaise's method [2]) leads, as already pointed out, to a substance containing both Mg and Zn.

The use of the disproportionation reaction seemed to us to be expedient:

$$R_2Zn + ZnX_2 \rightarrow 2RZnX, \qquad (I)$$

since it did not limit us in the selection of the radical (alkyl or aryl) or in the selection of the halide.

As we have shown in the present investigation, when a solution of R_2Zn in ether is added to an equivalent amount [Equation (I)] of a solution of zinc halide in the same solvent, a mixed organozinc compound of the type RZnX is formed. Recovery of the compound from solution as a compound having a definite formula was accomplished by the addition of dioxane to precipitate the crystalline complex $RZnX \cdot C_4H_8O_2$.

For the purpose of identification, this same compound was prepared by the direct action of alkyl halide on zinc, treatment of the solid material with ether, and precipitation from the ether solution with dioxane.

Moreover, as regards aromatic compounds, mixing at room temperature of ether solutions of, for example, diphenylzinc and an equivalent amount of zinc iodide and subsequent concentration of the solution gave crystalline mixed organozinc compounds in the form of complexes with, for example, ether; analysis of these compounds indicated the composition $ArZnX \cdot (C_2H_5)_2O$.

As regards the structures of these mixed organozinc compounds of definite composition, which were prepared by us for the first time, it can be stated that, first, the crystalline complexes obtained by disproportionation and by direct reaction between zinc and ethyl iodide were identical; second, (according to Krause and Fromm [6]) the action of a Grignard reagent on a solution of an organozinc compound (prepared from ethyl iodide and zinc) leads to unsymmetrical $RZnR_1$:

$$C_2H_5ZnI + R_1MgX \rightarrow C_2H_5ZnR_1 + MgXI \qquad (II)$$

and this quite indirectly indicates the composition of the original organozinc component to be RZnX.*

These mixed organozinc compounds were white crystalline substances, soluble in ether, dioxane, and acetoacetic ester and insoluble in benzene, hexane, carbon tetrachloride, and chloroform; they react violently with alcohol and water, for example, but are not air hypergolic, and are completely stable when stored in sealed vessels in an atmosphere of dry, inert gas. They do not inherently have a definite melting point (decomposition).

These crystalline substances react with acyl halides with the formation of the corresponding ketones.

$$C_2H_5ZnI \cdot C_4H_8O_2 + C_6H_5 \cdot COCl \rightarrow C_2H_5 \cdot CO \cdot C_6H_5 + ZnICl \cdot C_4H_8O_2. \qquad (III)$$

EXPERIMENTAL

All of the experiments described below were carried out in an atmosphere of dry nitrogen or argon in an apparatus previously developed in our laboratory during investigations in the field of organolithium compounds [7].

The zinc chloride and bromide were dried by distillation from a quartz retort. Anhydrous zinc iodide was prepared by the literature method.

The dioxane (1,4-dioxane throughout this paper) and ether were dried over sodium in the usual manner.

Mixed organozinc compound $C_2H_5ZnI \cdot C_4H_8O_2$ from diethylzinc and zinc iodide. Solutions of 2 g (1 mole) of diethylzinc in 15 ml of ether and 5 g (1 mole) of zinc iodide in 20 ml of the same solvent were mixed. On the addition of 10 ml of dioxane, a white crystalline precipitate formed; this was suction filtered, washed with cold petroleum ether, and dried under vacuum. 7.7 g of material was obtained (yield, 80% of theoretical).

This complex was similar in its properties to the complex obtained from zinc and ethyl iodide (see following experiment).

Found %: Zn 21.60; 21.64; I 41.11; 40.83 $C_6H_{13}ZnIO_2$. Calculated %: Zn 21.15; I 41.04

Mixed organozinc compound $C_2H_5ZnI \cdot C_4H_8O_2$ from zinc and ethyl iodide. 13 g of zinc-copper alloy (8% copper), in the form of turnings, was placed in a 300-ml flask fitted with a reflux condenser and a stirrer with a mercury seal; 15.6 g (1 mole) of ethyl iodide was added, and the reaction mixture was heated, with vigorous stirring, to the boiling point of the ethyl iodide. A vigorous reaction began after half an hour, and the entire reaction mixture congealed into a grey, solid mass, which was dissolved in 30 ml of ether and filtered, under nitrogen, through a funnel containing a No. 4 glass filter. 20 ml of dioxane was added to the filtrate, whereupon a

* Another possibility is to ascribe to the compounds obtained, by analogy to the organolithium ternary compounds studied by one of us and T. V. Talalaeva [7], the formula of the ternary complex $R_2Zn \cdot ZnX_2 \cdot 2C_4H_8O_2$ (with the appropriate ether). (Cf. also [4]).

white, crystalline precipitate formed. The precipitate was suction filtered, washed with cold petroleum ether, and dried under vacuum. 25.1 g of material was obtained (80.6% of theoretical, calculated on the ethyl iodide used).

Found %: Zn 21.25; 21.30; I 41.04; 41.30 $C_6H_{13}ZnIO_2$. Calculated %: Zn 21.15; I 41.04

Interaction of $C_2H_5ZnI \cdot C_4H_8O_2$ and benzoyl chloride. A suspension of 8 g of $C_2H_5ZnI \cdot C_4H_8O_2$ (1 mole) in 10 ml of dry toluene was charged to a 250-ml flask fitted with a stirrer with a mercury seal, a dropping funnel, a thermometer, and a reflux condenser. The contents of the flask were cooled to 5° by means of external cooling, and 2.4 g of benzoyl chloride (0.66 mole) was added dropwise; no increase in the temperature of the reaction mixture was observed during the addition of the benzoyl chloride. The cooling bath was removed, and the mixture was stirred at room temperature until the odor of benzoyl chloride disappeared (about half an hour). After decomposition with water, the toluene layer was separated, and the water layer was extracted with toluene. The toluene solution was washed with water, dilute ammonia, and again with water and dried over calcined potassium carbonate. The toluene was distilled leaving 0.72 g of substance with a boiling point of 215° (the boiling point of ethyl phenyl ketone is 218°). The yield was 31.3% (calculated on the benzoyl chloride used).

Mixed organozinc compound $p\text{-}CH_3C_6H_4ZnBr \cdot (C_2H_5)_2O$ from di-p-tolylzinc and zinc bromide. Solutions of 1.5 g (1 mole) of di-p-tolylzinc in 10 ml of ether and 1.3 g (0.95 mole) of zinc bromide in the same volume of the same solvent were mixed (a slight turbidity formed during mixing). One-third of the solvent was distilled under vacuum and the resulting white, crystalline precipitate was suction filtered and dried under vacuum. 2.6 g of material was obtained (yield 72.5% of theoretical).

Found %: Zn 21.20; 21.44; Br 25.76; 26.05 $C_{11}H_{17}ZnBrO$. Calculated %: Zn 21.08; Br 25.74

Mixed organozinc compound $C_6H_5ZnI \cdot (C_2H_5)_2O$ from diphenylzinc and zinc iodide. Solutions of 1.1 g (1 mole) of diphenylzinc in 10 ml of ether and 1.55 g (1 mole) of zinc iodide in 10 ml of the same solvent were mixed and allowed to stand for a period of several hours (a slight turbidity formed when the solutions were poured together, but this disappeared on standing). A considerable part of the solvent distilled under vacuum, and the resulting white, crystalline precipitate was suction filtered and dried in a stream of nitrogen. 2.6 g of material was obtained (yield 79.0% of theoretical).

Found %: Zn 18.63; 19.16; I 36.67; 37.03 $C_{10}H_{15}ZnIO$. Calculated %: Zn 19.05; I 36.97

Interaction of $C_6H_5ZnI \cdot (C_2H_5)_2O$ and benzoyl chloride. A suspension of 11.3 g of $C_6H_5ZnI \cdot (C_2H_5)_2O$ (1 mole) in 30 ml of dry toluene was charged to a 200-ml flask fitted with a stirrer with a mercury seal, a dropping funnel, a thermometer, and a reflux condenser. The contents of the flask were cooled by external cooling (ice), and 3 g (0.66 mole) of benzoyl chloride was added dropwise in a manner such that the temperature of the reaction mixture did not exceed 5°; after addition of the benzoyl chloride was complete, the reaction mixture was stirred for an hour without cooling. After decomposition with water, the toluene layer was separated and treated in the usual manner. Distillation of the toluene gave 2.8 g of a substance with a melting point of 42-44° (without recrystallization; m.p of benzophenone, 48°). The yield was 72% of theoretical, calculated on the benzoyl chloride charged.

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COMPLEX FORMATION OF Np^{4+} AND NpO_2^+ WITH TRILON B IN AQUEOUS SOLUTIONS

A. D. Gel'man and M. P. Mefod'eva

Institute of Physical Chemistry, Academy of Sciences, USSR

(Presented by Academician V. I. Spitsyn, July 7, 1958)

The interaction of actinides with Trilon B* has been investigated by a series of authors [1-4] over the last few years. However, there are no data in the literature on complex formation of neptunium with this addend. We attempted to fill in this gap as far as possible.

Complex formation of Np (IV) was investigated in hydrochloric acid solution containing 0.3 M $N_2H_4 \cdot HCl$ and complex formation of Np (V) in nitric acid solution.** The ionic strength μ was kept constant by the addition of KCl and KNO_3, respectively.

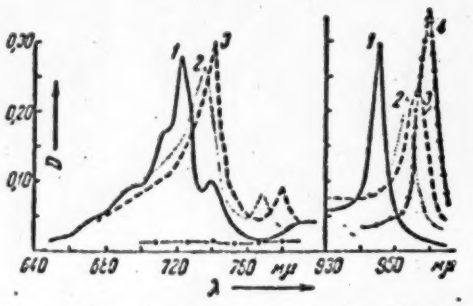

Fig. 1. Absorption curves: 1) solution of Np(IV) in 1 N HCl; 2) solution with equivalent amounts of neptunium and Trilon at pH 1.1; 3) solution containing a 10-fold excess of Trilon with respect to Np (IV) at pH 4.8; 4) solution containing a 10-fold excess of Trilon at pH 9.

The neptunium content was determined by spectrophotometric titration (by A. A. Chalkhorskii's method, with an accuracy of ± 3%). The Trilon B solution was prepared from doubly recrystallized acid. The optical density, D, was measured on an SF-4 spectrophotometer. The acidity of the solution was determined either by titration or by measurement on an LP-5 potentiometer.

Complex formation of Np^{4+} with Trilon B. The addition of excess Trilon B to an Np (IV) solution at ph 5.5 displaces the absorption intensity toward longer wavelengths, so that instead of a maximum at 722 mμ, a maximum at 740 mμ appears and a maximum at 780 mμ is also produced. The maximum at 960 mμ is displaced to 983 mμ. An increase in the pH to 6.8 led to fall in the maxima at 740 and 780 mμ and a maximum appeared at 988 mμ instead of the maximum at 983 mμ. Reducing the pH to 5.2 reversed this process.

When the pH was reduced below 3, the displacements of the maxima in the complex spectra were as follows: 740 mμ→736 mμ; 780 mμ→768 mμ; 983 mμ→976 mμ (Fig. 1).

*Trilon B is the disodium salt of ethylenediaminetetraacetic acid $(HOOC-CH_2)_2-N-(CH_2)_2-N-(CH_2COOH)_2$, usually denoted by H_4Y or EDTA.

** Complex formation of Np^{4+} with Cl^- in 1 M HCl is extremely slight and was neglected; the same is true for NpO_2^+ and NO_3^-.

Fig. 2 shows two plateaus •: 1) in the range from 0.5 N HCl to pH 2; 2) from pH 3.5 to pH 6.5.

Apparently, in each of these ranges the formation of some one complex compound predominates. The formation of an Np^{4+} complex with Trilon occurs even in 2.17 N HCl, since the values of $\bar{\epsilon}$ •• at 736 and 976 mμ are high in comparison with the spectrum of Np^{4+}. We should note that over the whole acidity range from 2.17 N HCl to pH 2, there are no other maxima besides those at 736, 768 and 976 mμ.

TABLE 1

Calculations of Stability Constant for the Complex of Np^{4+} with Trilon ($\epsilon_m = 40$; $\epsilon_k = 127$; $\lambda = 736$ mμ)

Acidity •	μ	•• $C_m \cdot 10^4$	D_{736}	$\bar{\epsilon} \cdot 10^4$	$C_{Trilon} \cdot 10^4$	$(C_{Tril} - C_c) \cdot 10^4$	$[H_mY]$	$[H_nY]$	K $[NpH_mY]^{n+}$	K $[NpH_nY]^{n+}$
2,17 N	2	9,88	0,553	1,6	66,6	65,0	$2,94 \cdot 10^{-6}$	$2,9 \cdot 10^{-6}$	$6,6 \cdot 10^{9}$	$6,68 \cdot 10^{9}$
1,3 N	2	15,28	0,091	4,36	66,6	62,24	$7,81 \cdot 10^{-7}$	$4,74 \cdot 10^{-6}$	$6,29 \cdot 10^{9}$	$1,03 \cdot 10^{9}$
0,94 N	1	10,29	0,081	4,72	20,0	25,28	$6,16 \cdot 10^{-6}$	$2,71 \cdot 10^{-6}$	$1,31 \cdot 10^{9}$	$2,97 \cdot 10^{9}$
0,891 N	1	10,29	0,122	9,3	66,6	57,3	$1,53 \cdot 10^{-7}$	$6,36 \cdot 10^{-6}$	$6,15 \cdot 10^{9}$	$1,48 \cdot 10^{9}$
0,665 N	2	10,7	0,123	9,24	66,6	57,36	$2,73 \cdot 10^{-7}$	$8,5 \cdot 10^{-6}$	$2,32 \cdot 10^{9}$	$7,44 \cdot 10^{9}$
0,5 N	1	20,8	0,225	16,38	20,3	3,92	$3,29 \cdot 10^{-6}$	$7,68 \cdot 10^{-6}$	$1,16 \cdot 10^{9}$	$5,08 \cdot 10^{9}$
0,39 N	1	13,32	0,149	11,05	14,7	3,65	$5,0 \cdot 10^{-6}$	$9,11 \cdot 10^{-6}$	$9,78 \cdot 10^{9}$	$5,36 \cdot 10^{9}$
pH 1,05	1	22,6	0,249	20,17	22,0	1,63	$4,41 \cdot 10^{-7}$	$1,83 \cdot 10^{-6}$	$1,88 \cdot 10^{9}$	$4,53 \cdot 10^{9}$
pH 1,16	1	22,6	0,273	21,02	22,0	0,98	$3,8 \cdot 10^{-7}$	$1,23 \cdot 10^{-6}$	$3,51 \cdot 10^{9}$	$1,08 \cdot 10^{9}$
							Mean ••• . . .		$(5,7 \pm 3,47) \cdot 10^{9}$	$(4,59 \pm 2,45) \cdot 10^{9}$ ••••

• In all experiments, [Cl⁻] equalled 1 N. Increasing the acidity and μ above 1 was accomplished by adding $HClO_4$ and $NaClO_4$.

•• In all the tables, the concentrations are expressed in moles per liter.

••• For $\mu = 1$.

•••• The results are similar for $\lambda = 976$ mμ.

Thus, spectrophotometric data indicate the predominant formation of only one complex compound over this range. In investigations at pHs above 2, it was necessary to consider the hydrolysis and disproportionation of Np^{4+}.

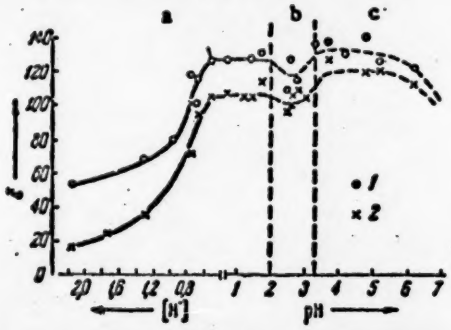

Fig. 2. Dependence of $\bar{\epsilon}$ of main Np (IV) maxima in the presence of excess Trilon on medium. Maxima for a: 1) 736 mμ, 2) 976 mμ; for b: 1) 738 and 739 mμ, 2) 980, 981 and 982 mμ; for c: 1) 740 mμ, 2) 983 mμ.

The composition of the complex, i.e. the ratio $[Np^{4+}]/[Trilon]$, was determined by spectrophotometric titration of Np^{4+} solution with Trilon (at constant acidity and with $\mu = 1$). The titration curves, showing the dependence of $\bar{\epsilon}$ of the main maxima on the ratio [Np]/[Trilon] in solution, have a break at the ratio 1:1, changing into a plateau, which indicates the formation of quite a stable [5] complex compound with the given composition. Similar curves were obtained for 0.5 N HCl and for a solution with pH 1.1.

We attempted to calculate the concentration stability constant $K = [NpH_mY^{m+}]/[Np^{4+}][H_mY^{-4+m}]$. The formation of complexes with compositions other than [Np]/[Trilon]=1:1 was excluded both on the basis of titration data and as a result of calculations based on the formula $K = C_c/(C_m - C_c)(C_{Tril} - nC_c)^n$, where C_c is the concentration of complex ion in the equilibrium solution, C_m, the total concentration of

• The dotted line indicates the approximate character of the curve.

•• $\bar{\epsilon}$ is the average molar absorption coefficient; $\bar{\epsilon} = D/C$ (mole/liter).

neptunium and C_{Tril}, the total concentration of Trilon.

The concentration of free Np^{4+} ion was found by difference $C_m - C_c$ and C_c calculated from the value D by the formula $C_c = D - \epsilon_m C_m / \epsilon_c - \epsilon_m$ for the two wavelengths 736 and 976 mμ. ϵ_m and ϵ_c are the molar absorption coefficients of Np^{4+} and the complex. The values of ϵ_c were taken from the graph (Fig. 2.). ϵ_m was determined by measurements of Np^{4+} solutions, not containing Trilon (with the same acidity and $\mu = 1$). The concentration of each EDTA anion was calculated from formulas in the literature [3].

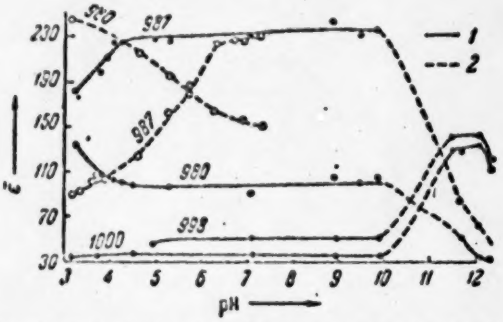

Fig. 3. Dependence of $\bar{\epsilon}$ of some absorption bands of Np (V) on pH.
1) With 200-fold excess of Trilon; 2) with a ratio of 1 : 1.

The stability constants were calculated for all complexes, which could be formed in the system (with the condition that only one was present at one time). As Table 1 shows, the value of the constant is most invariable over the whole acidity range for $[NpH_3\gamma]^{3+}$ and $[NpH_2\gamma]^{2+}$.

As already noted, the experimental data do not make it possible to identify the presence of two different complexes. An attempt to solve a system of two equations of the type $C'_c/(C_m - C'_c) K_1[H_3\gamma^-]' + K_2[H_2\gamma^{2-}]'$, on the assumption that both $[NpH_3\gamma]^{3}$ and $[NpH_2\gamma]^{2+}$ are formed simultaneously, was also unsuccessful; this indicates the implausibility of this assumption. However, on the basis of the great stability of the complex formed, as indicated above, and comparison with data on complex formation of other elements with Trilon, we are inclined to think that the predominant complex is $[NpH_2\gamma]^{2+}$ with $K = (5.7 \pm 3.47) \cdot 10^{17}$.

Complex formation of NpO_2^+ with Trilon B. Three series of experiments were performed in the investigation of complex formation by Np (V).

In series I, NpO_2^+ was titrated spectrophotometrically at pH 5.5 with a solution of Trilon ($\mu = 1$). The pH was kept constant by the addition of alkali and checked by the light absorption of Methyl red [6]. The absence of Np (IV) from the solution was verified by the spectrum in the region 700–740 mμ. The titration curve indicates

TABLE 2

Calculations of the Stability Constant for the Complex of NpO_2^+ with γ^{4-} with a 200-fold Excess of Trilon
($\mu \approx 0.1$; $C_m = 5.56 \cdot 10^{-4}$ $C_{Tril} = 0.1$ M; $\epsilon_m = 89$; $\epsilon_c = 230$)

pH	$D_{изм}$	$C_c \cdot 10^4$	$[\gamma^{4-}]$	$K_{[NpO_2\gamma]^{3-}}$
3,5	0,107	4,08	$3,29 \cdot 10^{-11}$	$8,4 \cdot 10^{16}$ *
3,8	0,113	4,5	$1,42 \cdot 10^{-10}$	$2,09 \cdot 10^{16}$
4,0	0,119	4,93	$3,01 \cdot 10^{-10}$	$2,17 \cdot 10^{16}$
4,2	0,124	5,28	$9,15 \cdot 10^{-10}$	$2,06 \cdot 10^{16}$
4,4	0,126	5,43	$2,3 \cdot 10^{-9}$	$1,82 \cdot 10^{16}$
		Mean		$(2,26 \pm 0,36) \cdot 10^{16}$

* This was not taken into consideration in calculating the mean.

TABLE 3

Calculation of the Stability Constant for the Complex of NpO_2^+ with γ^{4-} with Equimolar Amounts in the Solution
($C_m = 5.56 \cdot 10^{-4}$, $C_{Tril.} = 5.6 \cdot 10^{-4}$; $\epsilon_m = 89$; $\epsilon_c = 230$)

pH	$D_{изм}$	$C_c \cdot 10^4$	$(C_{Tril.} - C_c) \cdot 10^4$	$[\gamma^{4-}]$	$K_{[(NpO_2)\gamma]^{3-}}$
3,25	0,051	0,288	5,31	$5,05 \cdot 10^{-14}$	$2,3 \cdot 10^{16}$
3,5	0,053	0,673	4,93	$1,62 \cdot 10^{-13}$	$2,34 \cdot 10^{16}$
3,8	0,056	1,25	4,35	$6,18 \cdot 10^{-13}$	$2,17 \cdot 10^{16}$
4,0	0,058	1,63	3,97	$14,32 \cdot 10^{-13}$	$2,15 \cdot 10^{16}$
4,4	0,062	2,4	3,2	$7,36 \cdot 10^{-12}$	$5,65 \cdot 10^{16}$ *
				Mean	$(2,24 \pm 0,08) \cdot 10^{16}$

* This was not taken into consideration in calculating the mean.

* For other complexes, the value of K changes by several orders.

the formation of only one complex of NpO_2^+ with Y^{4-}. Calculation of the stability constant was possible only for the complex $[NpO_2Y]^{3-}$ ($K=(3.73\pm1.79)\cdot10^9$).

In experiments of series II, the dependence of complex formation on pH (Fig. 3) was investigated with a large excess of Trilon. Apparently, complex formation is complete at pH 4.5; since from this value up to pH 10, no change in spectrum was observed: this indicates that only one complex is formed in this range. The value of K for $[NpO_2Y]^{3-}$ was calculated for pH 3.2-4.5. • The value $K=(2.26\pm0.36)\cdot10^{10}$ differed slightly from that found by titration, but this may be partly explained by a difference in the ionic strengths. It is interesting to note that the constant we found for $[NpO_2Y]^{3-}$ ($pK=10.3$), is close to the constant for $[PuO_2Y]^{3-}$ ($pK=10.2$) [4].

In experiments of series III, an investigation was made of the dependence of complex formation on pH for a solution with equimolar amounts of Np (V) and Trilon. As Table 3 shows, all the Trilon is already bound at pH 6.3. Doubling the Trilon content leads to an increase in $\bar{\epsilon}$ (from 225-226 to 235) without a noticeable change in the position of the maximum (by 0.5 mμ). In contrast to previous experiments, with a low Trilon content it was possible to calculate the constant for the dinuclear complex in the pH range 3.25-4.4 (see Table 3). Although we were unable to obtain spectrophotometric proof of the formation of $[(NpO_2)_2Y]^{2-}$, nonetheless, the high invariability of the constant calculated for $[(NpO_2)_2Y]^{2-}$ makes it incorrect to reject the possibility of its existence. Apparently, an unequivocal solution to the problem may be found by the use of other physicochemical methods and also the preparative method.

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• We were unsuccessful in attempt to calculate the constant, assuming any other composition for the complex.
•• In Russian.

THE ADDITION OF FULL ESTERS OF PHOSPHOROUS ACID TO p-BENZOQUINONE

V. A. Kukhtin and K. M. Orekhova

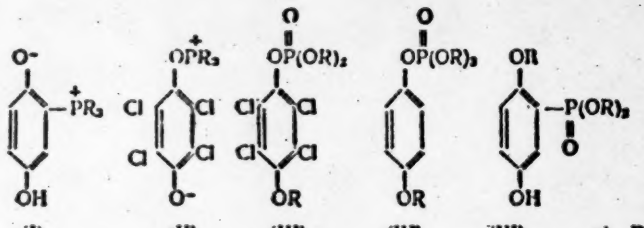
Kazan Branch of the All-Union Cinematographic Research Institute

(Presented by Academician B. A. Arbuzov, October 9, 1958)

In previous publications we described some new reactions of full esters of phosphorous and phosphinous acids with various π,π-conjugated systems – esters of α,β-unsaturated acids [1, 2], α,β-unsaturated aldehydes [3] and diacetyl [4]. These reactions proceed according to the Arbuzov rearrangement [2, 4].

In continuing the investigation of new forms of the Arbuzov rearrangement, we decided to study the reactions of phosphites with quinones.

Ramirez and Dershowitz [5] and later Hoffman, Horner and Hassel [6] showed that the product of adding triphenylphosphine to p-benzoquinone had the structure (I) and the products of interaction with chloranil, the structure (II).



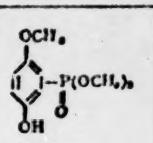
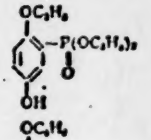
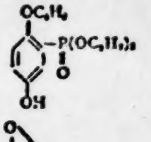
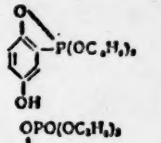
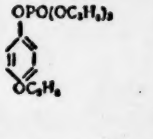
(I) (II) (III) (IV) (VI)

a) R = CH_3
b) R = C_2H_5
c) R = C_6H_7

As a result of reacting triethyl phosphite with chloranil, Ramirez and Dershowitz [7] obtained addition product with the structure (III). In a recently published paper [8], the same authors presented a new method of preparing monoalkyl ethers of hydroquinone, based on the hydrolysis of the addition products of trialkyl phosphites and p-benzoquinone, chloranil and other substituted p-benzoquinones. In the opinion of the authors, the addition products of trialkyl phosphites and p-benzoquinone have the structure (IV). Study of the paramagnetic resonance spectra of the reaction of chloranil with triethyl phosphite showed that this reaction apparently proceeds by a free radical mechanism [7].

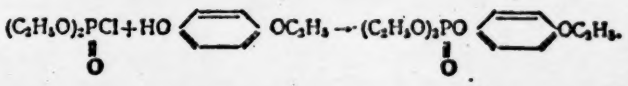
We prepared the addition products of some trialkyl phosphites and p-benzoquinone. The reaction was performed in dry benzene by the gradual addition of the trialkyl phosphite to p-benzoquinone solution. When the first drops of phosphite were added, the solution acquired a red color and the temperature gradually rose to 60–70°, when the reaction flask was cooled with water to prevent a further increase in temperature. At the end of the reaction the red color disappeared and the solution had the color of tea. The constants of the products we obtained are given in Table 1. When hydrolyzed in acid medium the addition products of trialkyl phosphites and p-benzoquinone gave hydroquinone as the main product. Hydrolysis with aqueous alcoholic alkali also caused

TABLE 1

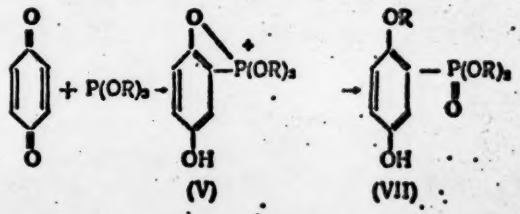
Expt. no.	Formula	B. p.	n_D^{20}	d_4^{20}	P, % found	P, % calc.	Yield %
1		162—163°/6 mm	1,4950	1,2423	13,04	13,27	51
2		162—163°/3 mm	1,4870	1,1531	11,38	11,31	65
3		175—176°/2 mm	1,4820	1,1416	9,99	9,81	53
4		M.p. 70—75° (with decomp.)	—	—	7,69	7,41	—
5		150—151°/3 mm	1,4805	1,1351	11,48	11,31	72

cleavage of the phosphorus part of the molecule. However, these facts still do not prove that the addition products have the structure (IV) since, as is know, the P–Ar bond is readily hydrolyzed if a hydroxy or an amino group is in a position ortho or para to the phosphorus [9]. The addition product of triphenylphosphine and p-benzoquinone (I) is readily hydrolyzed with the formation of hydroquinone and triphenylphosphine oxide [5, 6].

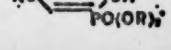
To prove the structure of the addition products of trialkyl phosphites and p-benzoquinone, we carried out a synthesis of diethyl p-ethoxyphenyl phosphate by the scheme:



The constants of the product obtained differed from those of the addition product of triethyl phosphite and p-benzoquinone (see Table 1). In addition, it did not have a free hydroxyl group, while in addition products, we were able to determine a hydroxyl group quantitatively [product (VI b); Calculated %: OH 6.2; Found %: OH 5.8]. These results indicate that in the addition products of trialkyl phosphites and p-benzoquinone, the phosphorus is apparently not connected to the oxygen but to the aromatic ring and like the addition products of triphenylphosphine and p-benzoquinone, they have the structure (VI) and not (IV).* The reactions of trialkyl phosphites with p-benzoquinone, probably proceed by the scheme:



(V) (VII)

*We cannot exclude the possibility that the addition products have the structure 

In contrast to trialkyl phosphites, triphenyl phosphite does not react with p-benzoquinone at room temperature. When benzene solution of triphenyl phosphite and p-benzoquinone was heated for a long time, the reaction mixture gradually acquired a dark red color and on the bottom of the flask appeared a precipitate, whose amount hardly changed during the reaction. After separation of the liquid part, the precipitate appeared as a white amorphous powder, which rapidly changed in air into a dark red tar with a phenolic smell. When heated in a sealed capillary it melted at 70-75° and was converted into a dark red tarry product. When the product obtained was treated with absolute ethyl alcohol, it also formed a dark red tar and liberated phenol.

In an attempt to distill the liquid part of the reaction products, it was only possible to distill a certain amount of phenol. Analysis of the product obtained for phosphorus showed that it was the addition product of one molecule of triphenyl phosphite and a molecule of benzoquinone. The chemical properties of the product obtained compel one to assume that it is the product of the first stage of the reaction of p-benzoquinone with triphenyl phosphite and has the structure (V).

In this case, the second stage of the Arbuzov rearrangement could not be achieved separately since it was accompanied by conversion of the reaction products to tar.

We should note that in the reaction of chloranil with triphenyl phosphite, Ramirez and Dershowitz were also unable to obtain the final reaction product (III); they obtained a readily hydrolyzable product, which, in their opinion, had the structure $(C_6H_5O)_3\overset{+}{P}O\langle\rangle O^-$. In studying the reaction of triethyl phosphite with p-benzoquinone by paramagnetic resonance, we were unable to observe the formation of free radicals during the reaction. When this reaction was carried out in the presence of diphenylpicrylhydrazine, it was also impossible to detect the formation of free radicals. The paramagnetic resonance spectrum of the reaction of chloranil with triethyl phosphite, which we repeated, had two clearly expressed peaks, agreeing with the description of Ramirez and Dershowitz, which confirms the formation of free radicals during this reaction.

The paramagnetic resonance spectra were obtained at our request by N. S. Garif'yanov and the authors are very grateful to him.

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THE STRUCTURE OF ERYSIMOSIDE – A STEROID DIGLYCOSIDE FROM PLANTS OF THE SPECIES ERYSIMUM

V. A. Maslennikova, F. S. Khristulas and N. K. Abubakirov

Institute of Plant Material Chemistry, Academy of Sciences, Uzbek SSR

(Presented by Academician M. M. Shemyakin, October 2, 1958)

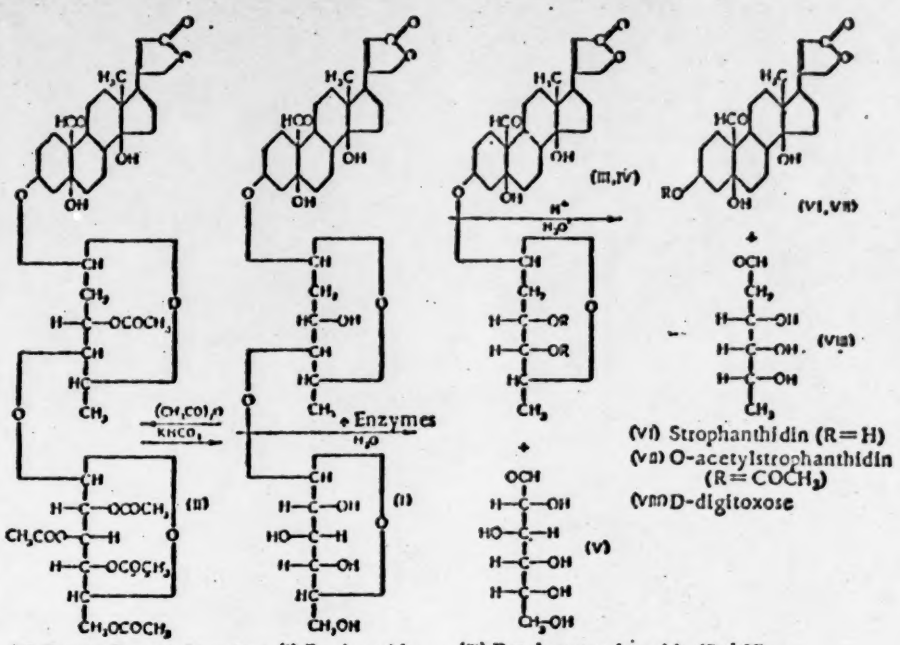
Plants of the species Erysimum (celandine) have been studied for steroid glycosides in them only comparatively recently. Pharmacological investigations have been accomplished most successfully and these led to the discovery of a series of plants, extracts from which possessed activity, specific for cardiac glycosides [1-4]. The chemical study of the active principles of celandines stagnated somewhat and has only been pursued vigorously in recent years. From early papers [5, 6] it was known that substances with the character of lactones were present in celandines and these were apparently the aglycones of glycosides and Feofilaktov and Loshkarev [7, 8] were the first to isolate an authentic glycoside, called erysimine, from Erysimus canescens. Recently the glycoside helveticoside has been found in E. crepidifolium and E. helveticum [9] and erysimotoxin has been found in E. cheiranthoides [10]. All three glycosides – erysimine, helveticoside and erysimotoxin – are monoglycosides.

We made a chemical investigation of the steroid glycosides of Erysimum growing in Central Asia – E. diffusum Ehrh., E. Gypsaceum Bosch. et Vved., E. Marschallianum Andrz., E. repandum L., E. violascens M. Pop., E. vitillinum M. Pop. This report gives data from work with the seeds of E. diffusum Ehrh., although similar glycosides were detected by paper chromatography in other forms of Erysimum. Two extraction methods were tried. Since specific enzymes present in the plants could cause hydrolytic cleavage of the extracted glycosides during the extraction process if this were not prevented, so that it would not be possible to obtain the glycosides in an unchanged form, in the first variation a method was used which prevented the action of enzymes as far as possible. In the second variation, the crude material was subjected to fermentation. The qualitative composition of the glycosides at the different stages of the work was controlled by paper chromatographic analysis.

In the first case, i. e., when the action of hydrolyzing agents was excluded, the position of the biggest spot on the chromatogram of the mixture of glycosides corresponded to the place at which one usually finds diglycosides of the olitoroside type [11] (R_f = 0.48 ± 0.02; system, toluene – butanol – water, 1:1:1; developer – Raymond or Kedde reagents; "rapid" chromatography paper of No. 2 Factory, Leningrad). After a long and multistage separation (the method of isolation and purification of the glycosides will be presented in another place), the substance moving similarly to olitoroside was isolated and it gave a single spot on a chromatogram. The new glycoside was called erysimoside (I). Elementary analysis of erysimoside lead to the formula $C_{35}H_{52}O_{14}$.

Found %: C 60.37; H 7.74 $C_{35}H_{52}O_{14}$. Calculated %: C 60.33; H 7.52

Erysimoside is a colorless, amorphous powder with a specific rotation $[\alpha]^{20}D = +16.5° \pm 1°$ (concentration 2.37 in methanol). It dissolves readily in methyl and ethyl alcohols, quite readily in water, sparingly in chloroform and is insoluble in ether. Erysimoside gives all the color reactions characteristic of cardiac glucosides of the digitalis – strophanthus group: Legal, Balet, Raymond, Kedde, Frercjaeques and Diurzh – and also the Liebermann reaction, characteristic of steroids. The color reaction with 84% sulfuric acid changes in the following way with time: 0 min. – green, 1 min. – dark green, 2 min. – brownish green, 30 min. – brown and 1 hour – brown.



(II) Penta-O-acetylerysimoside

(I) Erysimoside

(III) Desglucoerysimoside (R = H)

(IV) Di-O-acetyldesglucoerysimoside (R = $COCH_3$)

(V) D-glucose

(VI) Strophanthidin (R = H)

(VII) O-acetylstrophanthidin (R = $COCH_3$)

(VIII) D-digitoxose

On standing for several days with acetic anhydride in pyridine solution, erysimoside gives a readily crystallizable acetyl derivative with m.p. 221-223° (with decomp.) and $[\alpha]_D^{25} = 33.9° \pm 2°$ (concentration 1.80 in methanol). According to analysis, this compound is the pentaacetyl derivative (II).

Found %: C 59.68; 59.61; H 6.98; 6.81 $C_{45}H_{62}O_{13}$. Calculated %: C 59.69; H 6.89

The acetyl derivative is readily hydrolyzed with potassium bicarbonate in methanol, but this gives amorphous erysimoside (I).

The structure of erysimoside was established by stepwise hydrolysis. When treated with the pancreatic juice of the snail Helix plectotropis or an enzyme solution obtained from the seeds of E. diffusum, erysimoside loses a molecule of hextose and is converted into a monoglycoside. The sugar eliminated was identified as D-glucose (V) by paper chromatography and also the preparation of a crystalline osazone with m.p. 205°.

The part of the molecule left after removal of the glucose – desglucoerysimoside (III) crystallized from 60% methanol in the form of long, colorless needles. Elementary analysis of the compound corresponded to the formula $C_{29}H_{42}O_9$.

Found %: C 64.97; 64.93; H 8.00; 8.11 $C_{29}H_{42}O_9$. Calculated %: C 65.15; H 7.92

As with the most cardiac glycosides, the melting point of desglucoerysimoside was not constant. After many recrystallizations and drying over phosphorus pentoxide at room temperature, the desglucoerysimoside had m.p 174-175° and $[\alpha]_D^{25} = +32.4° \pm 2°$ (concentration 2.54 in methanol). The same sample had m.p. 152-155° after several hours drying in vacuum at 105-110°, as is usually done before analysis.

Desglucoerysimoside is readily soluble in methanol, ethanol and chloroform, slightly soluble in cold and readily soluble in hot water, and almost insoluble in ether and benzene. The glycoside gives color reactions, characteristic of cardiac glycosides with five-membered lactone rings. A positive Keller–Kiliani reaction indicated that the aglycone is attached to a 2-desoxy sugar. In 84% sulfuric acid, the glycoside dissolves to give a brown color, which changes to green after 5 hours. In the toluene – butanol – water system (1 : 1 : 1), desglucoerysimoside moves almost identically with strophanthidin (R_f 0.85 ± 0.02), therefore, to discriminate between them better, we used the system chloroform–toluene (1 : 1), saturated with formamide, and a hard chromatography paper.

When heated with acetic anhydride in pyridine at 100° for 3 hours, desglucocerysimoside forms a diacetyl derivative (IV) with m.p. 242-243° and $[\alpha]^{20}D$ + 35.5° ± 2°(concentration 2.57 in chloroform).

Found %: C 63.77, 63.88; H 7.66; 7.64 $C_{33}H_{46}O_{11}$. Calculated %: C 64.03; H 7.53

Attempts to prepare any carbonyl group derivatives (phenylhydrazone, oxime and semicarbazone) were unsuccessful.

Mild acid hydrolysis of desglucocerysimoside led to cleavage of the second sugar molecule. The aglycone (VI) thus formed was recrystallized from alcohol and ether to give rhombic prisms with m.p. 176-177°, $[\alpha]^{19}D$ + 48.6° ± 2° (concentration 2.61 in methanol).

Found %: C 67.17; 67.13; H 8.10; 8.14 $C_{23}H_{32}O_6 \cdot 0.5\ H_2O$. Calculated %: C 66.80; H 8.04

This compound gave a monoacetyl derivative $C_{25}H_{34}O_7$ (VII) with m.p. 243° and a crystalline phenylhydrazone with m.p 241-242°. The aglycone of desglucocerysimoside was identified as strophanthidin by mixed melting points with the derivatives obtained and comparison of the movement on a paper chromatogram.

The sugar component, remaining in the mother solution after cleavage of the strophanthidin, was isolated and condensed with p,p'-nitrobiphenylsulfonylhydrazine by the method proposed by Westphal et al.[12].* After recrystallization from acetonitrile, the sulfonylhydrazone obtained had m.p 155-156° and m.p. 138-139° after recrystallization from methanol, which agree with constants of the condensation product of p,p'-nitrobiphenylsulfonylhydrazine and D-digitoxose (VIII).

Comparison of the molecular rotations of erysimoside, desglucocerysimoside and strophanthidin, shows that in accordance with Klyne's rule [13], the sugar is attached by a β-glycoside link in both places. Thus, erysimoside is strophanthidin (3)-β-D-digitoxoside-β-D-glucoside; its structure is represented by formula (I). Erysimoside and olitoroside [11] are diastereoisomeric compounds.

In the second variation of the extraction, when the seeds were steeped in water in a thermostat at 37° for 3 days, as would be expected, the main part of the mixture of glycosides was desglucocerysimoside.

Since desglucocerysimoside and the previously described helveticoside [9] and erysimotoxin [10] have the same chemical structure, they must be considered as identical, despite slight differences in their physicochemical constants.

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SYNTHESIS OF 2,4,4-TRIMETHYL-3-tert-BUTYLPENTENE-2 (THE β-FORM OF BUTLEROV'S TRIISOBUTYLENE)

A. P. Meshcheryakov and E. I. Erzyutova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

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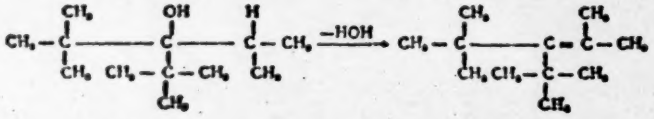
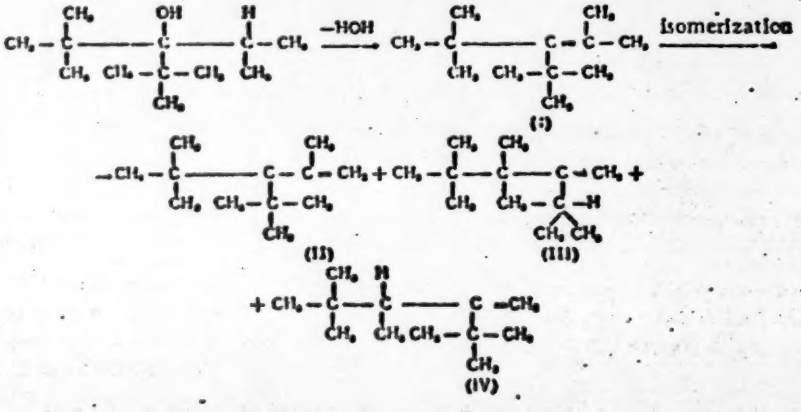
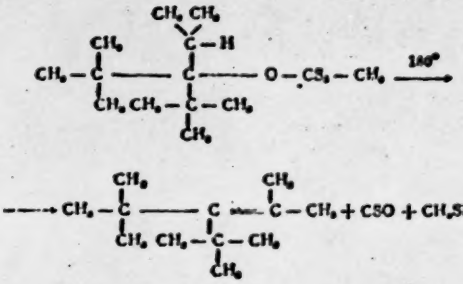
Triisobutylene was first prepared by A. M. Butlerov from isobutylene in the presence of sulfuric aicd [1]. A. M. Butlerov ascribed the structure of 2,4,4-trimethyl-3-tert-butylpentene-2 to triisobutylene. However, subsequent investigaters ([2-4] and others) showed that triisobutylene was a mixture of four isomers: 1,1-dineopentylethylene (56%), 2,2,4,6,6-pentamethylheptene (34%), 2,4,4,6,6-pentamethylheptene-2 (5%) and 2,4,4,6,6-pentamethylheptene-2 (5%). Thus the question of the existence of the β-form of Butlerov's triisobutylene remained open until the present time and it seemed interesting to find a method of synthesizing this hydrocarbon and studying its properties. One possible method of synthesizing 2,4,4-trimethyl-3-tert-butylpentene-2 is the dehydration of di-tert-butylisopropylcarbinol.



We found that the dehydration of di-tert-butylisopropylcarbinol in an acid medium was accompanied by isomerization of the primary dehydration product, which involved not only migration of the double bond from a β- to α-position, but also a skeletal change in the alkene obtained. Our experiments on dehydration of the alcohol, 1) by Zigler's method [5], 2) under the action of HCl at −30° and 3) over Al_2O_3 at 220° (150 mm Hg pressure), invariably led to the formation of a mixture of α-alkenes, consisting predominantly of 3,3,4,4-tetramethyl-2-isopropylpentene-1 (obtained by Bartlett) and 2,4,4-trimethyl-3-tert-butylpentene-1 and possibly containing 3,4,4-trimethyl-2-tert-butylpentene-1 also.



To eliminate skeletal isomerization during dehydration of the alcohol, we used L. A. Chugaev's xanthate method [6].



It was only in the dehydration of di-tert-butylisopropylcarbinol by the xanthate method that we were able to obtain the normal dehydration product, 2,4,4-trimethyl-3-tert-butylpentene-2 (the β-form of Butlerov's triisobutylene) for the first time together with isomers (II), (III) and (IV). The presence of this hydrocarbon was proved by oxidation. The oxidation yielded acetone and hexamethylacetone.

EXPERIMENTAL

Di-tert-butylisopropylcarbinol was obtained by two methods: 1) the reaction of tert-butyllithium and pentamethylacetone at a temperature from −60 to −70° [4]; 2) by a one-stage method, whose conditions we worked out and in which metallic lithium was added to an equimolecular mixture of tert-butyl chloride and pentamethylacetone at 20-30°. Constants of the alcohol: b.p. 120-122°/28-29 mm; d^{20}_4 0.8662; $n^{20}D$ 1.4650; MR calculated 59.13, found 59.32.

Found %: C 77.1; 77.2; H 13.9; 14.1 $C_{12}H_{26}O$. Calculated %: C 77.9; H 14.0

Literature data: b.p. 120°/30 mm; $n^{20}D$ 1.4665 [7]. Found: H_{active} 1.18; 1.10.

The dehydration of di-tert-butylisopropylcarbinol over Al_2O_3 was carried out in a catalytic furnace at 200-220° in vacuum (15 mm). Properties of alkene obtained: b.p. 83-84°/28 mm; d^{20}_4 0.8222; $n^{20}D$ 1.4577, MR calculated 57.15, found 55.83.

Found %: C 85.51; 85.34; H 14.11; 14.01 $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37

The dehydration by Zigler's method was carried out in glacial acetic acid with several drops of concentrated H_2SO_4 added by heating on a water bath for 30 min. The olefin had: b.p. 87-88°/25 mm; d^{20}_4 0.8148; $n^{20}D$ 1.4520; MR found 55.75, calculated 57.19.

Found %: C 85.56; 85.44; H 14.31; 14.37 $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37

Dehydration with HCl at −30°. An alkene was obtained with b.p. 85-81°/28 mm; d^{20}_4 0.8165, $n^{20}D$ 1.4502; MR calculated 57.15, found 55.44.

Found %: 85.83; 85.73; H 14.31; 14.47 $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37

The olefins obtained were oxidized with 1% $KMnO_4$ solution at 20° for 20 days. Their oxidation proceeded very slowly and to complete it, the reaction mixture had to be heated on a water bath for 6 hours. Formic acid (detected by the calomel method) was isolated from the acid oxidation products. This indicated the presence of only α-alkenes in this mixture, as was confirmed by the characteristic frequency (1625 cm^{-1}) in the Raman spectra.

The mixture of alkenes, obtained by dehydration according to Zigler's method and over Al_2O_3, was hydrogenated in n-pentane solution in a rotating autoclave over Bag's catalyst at 180° and a pressure of 200 atm. Properties of the alkanes: b.p. 200-201°/757 mm and 100-101°/32 mm; d^{20}_4 0.7988; $n^{20}D$ 1.4492; MR found 57.2, calculated 57.61.

Found %: C 84.34; 84.38; H 15.65; 15.45 $C_{12}H_{26}$. Calculated %: C 84.61; H 15.39

The viscosity at 20° was 3.88 centistokes and the solidification point −70°.

Dehydration of alcohol by the xanthate method of Chugaev [6]. The potassium alcoholate was prepared from 60 g of alcohol and converted into the xanthate by treatment with carbon disulfide. Treatment of the salt with methyl iodide gave 25 g of the xanthate ester. Its constants were as follows after vacuum distillation (10 mm): b.p. 135-140°/30 mm; d^{20}_4 0.9576; $n^{20}D$ 1.4926.

Found %: C 61.98; 61.93; H 10.56; 10.55; S 19.4; 19.5 $C_{14}H_{28}OS_2$. Calculated %: C 60.8; H 10.27; S 23

From the analysis it follows that the xanthate ester obtained partly decomposed during distillation and contained a small amount of olefin. The xanthate ester was subjected to thermal decomposition on an oil bath at 180°. The decomposition yielded 8 g of olefin, which had the following constants after several distillations over sodium on a column in a stream of nitrogen: b.p. 83-84°/29 mm; d^{20}_4 0.8261; $n^{20}D$ 1.4585; MR found 55.66, calculated 57.15.

Found %: C 86.0; 85.99; H 14.18; 13.97 $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37

The olefin obtained was oxidized with a 1% aqueous solution of $KMnO_4$. The oxidation proceeded differently from the oxidation of the olefins obtained previously. It was complete at 20° after 9 hours. The rapid oxidation of the product obtained indicated that an alkene was present in it, which contained a double bond in the β-position [9].

Formic acid (detected by the calomel method) was isolated from the acid products of oxidation. The neutral oxidation products yielded acetone (identified as its semicarbazone with m.p. 185-186°, not depressed by admixture with an authentic sample). In addition, the neutral products yielded a fraction with b.p. 150-200° (mainly 150-160°). It was surmised that this contained hexamethylacetone. To prove this, Raman spectra were plotted for pure authentic hexamethylacetone and then for the fraction boiling at 150-200°, obtained in the oxidation. It was established that hexamethylacetone predominated in it.

Frequencies $\Delta\nu$ (in cm^{-1}): 360 (2 double), 410 (2 broad), 536 (3), 636 (10), 837 (7), 938 (5 double), 1449 (7), 1445 (4), 1692 (4) and others.

In addition, it was shown that the same mixture contained a significant amount of unoxidized alkene with a double bond frequency $\Delta\nu$ of 1625 cm^{-1} and a small amount of an alkene with a double bond frequency $\Delta\nu$ of 1673 cm^{-1}. Thus, both the oxidation and the Raman spectrum showed that the mixture of alkenes, obtained by dehydration by the xanthate method, contained the alkene 2,4,4-trimethyl-3-tert-butylpentene-2, the β-form of Butlerov's trisobutylene.

Raman spectra of the alkenes and alkanes obtained ($\Delta\nu$, cm^{-1}).

1. The mixture of alkenes, obtained by dehydration of the alcohol using Zigler's method: 187 (2 broad), 244 (0 broad), 413 (3 broad), 490 (0 broad), 546 (5), 632 (8), 678 (6), 704 (0), 751 (0), 820 (5), 860 (6 broad), 895 (1), 910 (2), 927 (6), 953 (1), 980 (0), 1024 (0), 1047 (0), 1083 (4), 1104 (4 broad), 1202 (1), 1220 (5 broad), 1246 (1), 1285 (1), 1306 (0), 1341 (1), 1362 (0), 1420 (2 broad), 1445 (3 broad), 1470 (4 broad), 1625 (5), 2866 (5), 2904 (8), 2927 (5 broad), 2968 (10 broad), 2987 (10 broad), 3080 (5).

2. The mixture of alkenes obtained by dehydration of the alcohol under the action of HCl at −30°: 148(4), 184 (3), 240 (0), 309 (0), 368 (0), 416 (1 broad), 497 (2 broad), 544 (6), 612 (0), 632 (10), 676 (9), 703 (1), 754(2), 818 (8), 855 (9), 894 (1), 907 (3), 925 (9), 954 (1), 1021 (2), 1045 (0), 1083 (5), 1098 (5 broad), 1155 (1 broad), 1201 (5) 1218 (8), 1246 (2), 1306 (2), 1337 (2), 1360 (2), 1393 (1), 1418 (3), 1443 (8), 1468 (8 broad), 1625 (8), 2868 (5), 2903 (8), 2926 (4 broad), 2966 (10 broad), 2986 (7 broad) 3080 (4).

3. The mixture of alkenes obtained by dehydration of the alcohol over Al_2O_3: 149 (2), 209 (0), 333 (0), 489 (0), 530 (0), 605 (1), 635 (6), 678 (1), 738 (2), 789 (1), 823 (1), 838 (1), 859 (2), 877 (0), 905 (2), 924 (3), 955 (0), 1019 (0), 1041 (0), 1106 (0), 1136 (0), 1202 (2), 1218 (2), 1254 (0), 1319 (0 broad), 1364 (0), 1383 (0), 1413 (2), 1444 (4), 1467 (4 broad), 1625 (5), 2869 (5), 2913(8 broad), 2961 (7), 2994 (6), 3082 (1).

4. The mixture of alkenes obtained by dehydration of the alcohol by Chugaev's xanthate method: 148 (3), 210 (2 broad), 339 (2 broad), 390 (3), 432 (0), 457 (0), 486 (0), 510 (0), 528 (1), 570 (3), 610 (2), 635 677 (2), 719 (0), 739 (6), 764 (2), 796 (3), 821 (5), 838 (5), 859 (8), 872 (1), 904 (8), 927 (8 broad), 951 (1),

986 (1), 1015 (1), 1042 (2 broad), 1082 (0), 1108 (1), 1140 (1), 1202 (7 broad), 1223 (7), 1262 (0), 1304 (2), 1323 (3 broad), 1361 (2), 1382 (1), 1415 (7), 1442 (10 broad), 1465 (10 broad), 1627 (10), 1671 (1), 2865 (8), 2880 (2), 2904 (9), 2930 (2), 2962 (9 broad), 2988 (8 broad), 3082 (5).

5. Spectrum of alkanes: 148 (1), 164 (0), 427 (1 broad), 289 (0), 324 (0), 353 (0), 422 (0), 437 (4), 467(1), 495 (1), 515 (0), 571 (5), 621 (0), 673 (4), 678 (6), 697 (0), 728 (0), 750 (1), 806 (7), 848 (8), 897 (7), 929 (9), 949 (2), 977 (3), 999 (1), 1022 (2), 1043 (0), 1063 (1 broad), 1097 (2), 1128 (0), 1173 (3 broad), 1215 (2), 1225 (0), 1252 (0), 1286 (4), 1308 (0), 1308 (0), 1342 (2), 1359 (0), 1381 (2), 1399 (2), 1424 (0), 1443 (10), 1469 (9 broad), 2867 (7), 2908 (9), 2951 (5), 2973 (8), 3061 (0), 3086 (0).

The presence in the mixture of alkenes, obtained by the different methods, of alkenes containing in the molecule two adjacent quaternary carbon atoms (the hydrocarbon 3,3,4,4-tetrabutyl-3-isopropylpentene-1) was confirmed by the frequencies 632 (8), 632 (10), 635 (6), and 635 (10) cm^{-1} and a double bond by the frequencies 1625 (5), 1625 (8), 1625 (5) and 1627 (10) cm^{-1}. The spectra of the alkenes, obtained by dehydrating the alcohol by the xanthate method, had the characteristic frequency 1671 (1) cm^{-1}, indicating a tetrasubstituted ethylene derivative, 2,4,4-trimethyl-3-tert-butylpentene-2, which was also confirmed by oxidation (isolation of acetone and hexamethylacetone).

The spectrum of the mixture of alkanes obtained had the frequencies 673 (4) and 678 (6) cm^{-1}, indicative of the two adjacent quaternary carbon atoms of 2,2,3,3,4,5-hexamethylhexane, the frequency 929 (9) cm^{-1}, characterizing the presence of quaternary carbon atoms at the end of the molecule's chain and the frequency 1173 (3 broad), indicating the presence of the isopropyl group of the molecule of 2,2,4,4-tetramethyl-3-isopropylpentane. Besides the frequencies given, there were also the frequencies 697 (0) and 728 (0) cm^{-1}, indicating the possible presence of 2,2,3,4,5,5-hexamethylhexane.

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DIFLUOROXYMOLYBDIC ACID

(SYNTHESIS AND PROPERTIES)

N. S. Nikolaev and A. A. Opalovskii

N. S. Kurnakov Institute of General and Inorganic Chemistry
Academy of Sciences, USSR

(Presented by Academician L. V. Tananaev, October 4, 1958)

Molybdenum (VI) is known to form a hexafluoride, MoF_6, and also oxyfluorides, molybdenum oxytetrafluoride, $MoOF_4$, and molybdenum oxydifluoride, MoO_2F_2. Molybdenum oxyfluorides are obtained by the action of anhydrous hydrogen fluoride on the appropriate oxychlorides [1]. The solution of molybdates in hydrofluoric acid or the addition of alkali metal fluorides to solutions of molybdenum trioxide in hydrofluoric acid gave many oxyfluoromolybdates, which may be considered as fluoro substituted derivatives of the corresponding molybdates [2]. The bulk of these lose fluorine when fired.

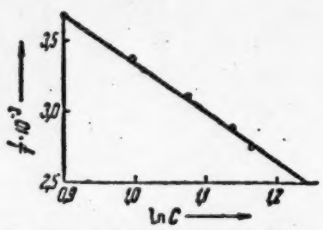

Fig. 1. Solubility of molybdic acid in hydrofluoric acid relative to temperature.

By studying the system $HF-MoF_6-H_2O$, using the isothermal solubility [3], the authors showed that the interaction of molybdenum trioxide with hydrofluoric acid led to the formation of an acido-complex compound – difluoroxymolybdic acid, $H_2MoO_3F_2 \cdot H_2O$, which occurs in the system both as a solid phase and as the compound in solution. The potassium salt of this acid, $K_2MoO_3F_2 \cdot H_2O$, was isolated by Smitz-Dumont and Opgengof [4] in their study of the behavior of molybdenum trioxide in potassium fluoride solution.

In the present communication, a method of synthesizing difluoroxymolybdic acid by the reaction of molybdic acid with hydrofluoric acid is presented and some of its properties are described

EXPERIMENTAL.

The temperature conditions of the synthesis were established relative to the solubility of molybdic acid in hydrofluoric acid. An increase in temperature produces an increase in the solubility of molybdic acid in hydrofluoric acid (see Table 1 and Fig. 1).

TABLE 1

Solubility of Molybdic Acid in Hydrofluoric Acid (starting solution – 40.3% HF)

Temp. °C	1000/T	MoO_3, wt. %	MoO_3, mole/liter (C)	ln C
0	3,66	35,41	2,46	0,9001
25	3,35	39,01	2,71	0,9970
50	3,09	42,03	2,92	1,0716
75	2,87	44,72	3,11	1,1347
90	2,75	46,11	3,20	1,1630

Thus, a method of synthesizing difluoroxymolybdic acid was planned, namely, the solution of molybdic acid in boiling hydrofluoric acid and crystallization of the difluoroxymolybdic acid by cooling.

Synthesis of difluoroxymolybdic acid. 100 g of doubly distilled hydrofluoric acid was heated to boiling in a platinum dish and 50 g of molybdic acid (analytical grade) added to form a saturated solution. The hot solution was filtered through platinum sponge in a platinum funnel to remove excess molybdic acid and cooled to room temperature. A colorless, crystalline precipitate separated on cooling. The precipitate was separated

Fig. 2. Microphotograph of difluoroxymolybdic acid crystals.

from the mother solution and washed twice with ethyl alcohol by decantation and then three times in a funnel with vigorous sucking off. The substance was dried at reduced pressure at a temperature of 50-60°.

The substance was analyzed for MoO_3 and HF contents by the method described previously [3]. The results of the analysis are presented in Table 2. For comparison, the Table also gives results obtained in analysis of the solid phase, $H_2MoO_3F_2 \cdot H_2O$, separated in the system $HF - MoF_6 - H_2O$ [3].

Properties of difluoroxymolybdic acid. Difluoroxymolybdic acid is a colorless, crystalline substance, which gradually decomposes in air with a color change from colorless to yellowish to greenish yellow. During storage in sealed ampules, similar color changes occur, but more slowly. When stored in Teflon vessels in vacuum, difluoroxymolybdic acid does not undergo changes. The form of the crystals is identical with that of those obtained previously in the system $HF - MoF_6 - H_2O$ (see Fig. 2) [3].

The solubility of difluoroxymolybdic acid in water at various temperatures was established.

Difluoroxymolybdic acid has a considerable solubility in water, which increases with an increase in temperature (see Table 3). From the data on the solubility of difluoroxymolybdic acid in water relative to temperature, it is possible to calculate the heat of solution according to Schröder's equation: $\ln C = \Delta H (T - T^*)/RTT^*$. It is also possible to use the graph of $C = \varphi (1/T)$ (see Fig. 3) for the calculations.

TABLE 2

Chemical Analysis of Difluoroxymolybdic Acid.

Preparation method	MoO_3, %	HF, %	H_2O, %	F: Mo
Prepared by synthesis	71.68	20.02	8.30	2.01
Prepared as a solid phase in the system $HF - MoF_6 - H_2O$	70.80	19.58	9.62	1.99
Calculated for the composition $H_2MoO_3F_2 \cdot H_2O$	71.28	19.81	8.91	2.00

The heat of solution of difluoroxymolybdic acid was found to be −0.4805 kcal/mole. In this case, the value refers to the heat of solution in a saturated solution (final heat of solution). However, since the Schröder equation is applicable under strictly defined conditions (extremely low solubility and in the absence of a chemical action of the solvent, which is not so in the case considered), the value obtained for the final heat of solution may be considered only as a qualitative characteristic of the thermal effect. This point of view is in accordance with the general premises of N. K. Voskresenskaya's work [5].

Thermal analysis of difluoroxymolybdic acid. Difluoroxymolybdic acid was subjected to thermographic examination. The heating curve (Fig. 4) showed three endo effects at temperatures of 290, 380 and 555°. To interpret the effects, the substance was kept at the appropriate temperature for an hour and then a sample analyzed chemically. Data from the chemical analysis are given in Table 4.

Difluoroxymolybdic acid did not decompose when heated to 290°. At 290° one molecule of water and 0.5

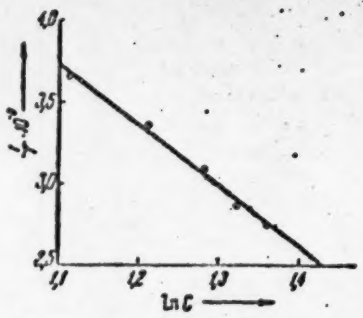

Fig. 3. Solubility of difluoroxymolybdic acid in water in relation to temperature.

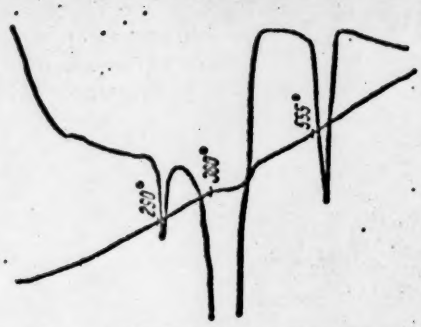

Fig. 4. Decomposition thermogram.

molecule of hydrogen fluoride were eliminated; thus, destruction of the complex acid occurred. At 380° there was further elimination of fluorine with the formation of a polyoxyfluoromolybdic acid with the composition $H_2Mo_4O_{13}F$. The potassium salt of a similar acid was prepared by Smitz-Dumont and Opgengof [4] as the unstable dehydration product of the compound $H_2Mo_4O_{13}F \cdot 3H_2O$.

TABLE 3

Solubility of Difluoroxymolybdic Acid in Water

Temp., °C	1000/T	MoO_3, weight %	MoO_3, mole/liter (C)	ln C
0	3.66	44.46	3.09	1.128
25	3.35	48.38	3.36	1.212
50	3.09	51.32	3.57	1.283
75	2.87	53.92	3.75	1.323
90	2.75	56.16	3.90	1.361

A further increase in the temperature to 555°, led to the formation of pure molybdenum trioxide. At this temperature, sublimation of the thermal decomposition product (molybdenum trioxide) occurred.

TABLE 4

Composition of Products Obtained in the Thermal Decomposition of Difluoroxymolybdic Acid, $H_2MoO_3F_2 \cdot H_2O$

Heating temperature, °C	Mo, %	F, %	F: Mo	Composition of compound
290	56.06	16.26	1.45	$H_2Mo_2O_6F_3$
380	64.46	3.02	0.24	$H_2Mo_4O_{13}F$
555	66.96	–	–	MoO_3

The thermal decomposition was accompanied by the formation as intermediate products of compounds, which may be considered as fluoro substituted isopolyacids. The results of thermographic analysis leads to the conclusion that the water, forming part of difluoroxymolybdic acid, is not hygroscopic, but part of the composition of the complex molecule.

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SYNTHESIS OF ORGANOMERCURY NITRO COMPOUNDS

S. S. Novikov, T. I. Godovikova and V. A. Tartakovskii

N. D. Zelinksii Institute of Organic Chemistry, Academy of Sciences, USSR

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As is known, many mercury salts of organic and inorganic acids find wide application in mercuration, addition to multiple bonds, etc. One may also surmise that mercury salts of the aci-form of nitroalkanes would also tend to undergo some of these reactions. Studies in this field were begun with an investigation of the mercury salt of trinitromethane as a substance in which tautomeric changes are especially clearly expressed [1].

We established that the mercury salt of trinitromethane readily mercurated compounds both of the aliphatic series, containing a labile hydrogen atom, and of the aromatic and heterocyclic series to form substances of the general formula $R-HgC(NO_2)_3$ by the scheme:

$$RH+Hg[C(NO_2)_3]_2 \rightarrow R-HgC(NO_2)_3+HC(NO_2)_3.$$

We studied this reaction in detail on the examples of malonic, acetoacetic and nitroacetic esters, acetylacetone, acetone, cyclopentanone, benzene, toluene, anisole, aniline, dimethylaniline, furan and thiophene.

The reaction conditions and constants, yields and analysis data of the final products are given in Table 1.

The structure of the organomercury nitro compounds synthesized was proved by substitution of the trinitromethyl residue by halide, when they were reacted with potassium halide:

$$R-HgC(NO_2)_3+KX \rightarrow R-HgX+KC(NO_2)_3.$$

When treated with bromine, the trinitromethylmercuriaryls formed the corresponding mercuribromides and bromotrinitromethane. Concentrated hydrochloric acid converted them into mercurichlorides:

$$Ar-HgC(NO_2)_3 \xrightarrow{Br_2} Ar-HgBr+BrC(NO_2)_3$$
$$Ar-HgC(NO_2)_3 \xrightarrow[HCl]{HCl} Ar-HgCl+HC(NO_2)_3$$

The ultraviolet spectra of the compounds we synthesized, plotted in polar and nonpolar solvents, differed sharply and agreed with spectra obtained by Hantzsch [2] for the mercury salts of trinitromethane in the corresponding solvents. This indicates that the mercuration products, like the mercury salt of trinitromethane itself, may exist in two interconvertible tautomeric forms, depending on the nature of the solvent:

$$R-Hg-C(NO_2)_3 \rightleftarrows R-Hg-O-N=C(NO_2)_2$$
$$\downarrow O$$

and in the crystalline state they are the actual organometallic compounds $R-Hg-C(NO_2)_3$.

The reaction of the mercury salt of trinitromethane with nitrobenzene, m-dinitrobenzene, o-nitrotoluene, and o-nitroanisole is extremely peculiar. Judging by the elementary analysis data and the chemical properties,

TABLE 1

Expt. no.	R*	Solvent	React. temp.	Reaction time, hour	M.p., °C	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
1	$HC(COOC_2H_5)_3$	ether	20	12	decomp. >250°	35	18,71 18,84	18,85	2,29 2,49	2,18	7,07 8,01	8,34
2	$HC(COOC_2H_5)(COCH_3)$	water	20	12	159	80	17,73 17,88	17,52	1,93 2,02	1,89	8,58 8,59	8,76
3	$HC(COOC_2H_5)(NO_2)$	water	20	0,25	135	98	12,33 12,38	12,44	1,22 1,31	1,25	11,27 11,19	11,69
4	$HC(COCH_3)_3$	water	20	12	158	85	15,98 16,23	15,82	1,55 1,62	1,57	8,92 8,94	9,34
5	CH_3COCH_3	water	20	50	153	98	12,05 12,08	11,78	1,40 1,44	1,24	10,16 10,19	10,31
6	C_3H_6O	water	20	60	140	95	16,57 16,70	16,61	1,73 1,77	1,63	9,55 9,62	9,89
7	C_6H_6	benzene	80	5	148	58,5	19,90 19,95	19,70	1,30 1,33	1,19	9,71 9,71	9,85
8	$CH_3C_6H_5$	toluene	80	3	*n* =140 *o* =120	51,5	21,45 21,77	21,75	1,70 1,73	1,59	9,59 9,49	9,54
9	$CH_3OC_6H_5$	alcohol	78	0,5	*n* =101 *o* =114	41	20,63 20,69	20,99	1,36 1,46	1,69	8,72 8,83	9,18
10	$C_6H_5NH_2$	alcohol	20	instant.	117	59	18,96 19,00	18,93	1,67 1,75	1,38		
11	$(CH_3)_2NC_6H_5$	alcohol	20	instant.	110	70						
12	C_4H_4O	ether	20	0,5	120	25	14,71 14,79	14,38	unstable 0,85 1,00	0,78	9,93 10,03	10,01
13	C_4H_4S	ether	20	0,5	115	28			unstable			

* General formula $RHgC(NO_2)_3$.

the substances obtained during the reaction are complex products of the addition of a molecule of the mercury salt of trinitromethane to the molecule of the particular nitroaromatic compound.

TABLE 2

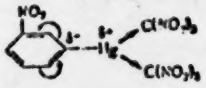
Formula	Reaction time, hour	M.p., °C	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$NO_2C_6H_4 \cdot Hg[C(NO_2)_3]_2$	3,5	118	55	15,50 15,67	15,40	0,81 0,91	0,80	15,54 15,48	15,72
$m\text{-}(NO_2)_2C_6H_3 \cdot Hg[C(NO_2)_3]_2$	3,5	147	60	14,41 14,45	14,72	0,94 0,80	0,61	—	—
$o\text{-}CH_3(NO_2)C_6H_3 \cdot Hg[C(NO_2)_3]_2$	3,5	75	55,5	16,82 17,06	16,84	0,87 0,95	1,10	—	—
$o\text{-}CH_3O(NO_2)C_6H_3 \cdot Hg[C(NO_2)_3]_2$	2	109	51	16,48 16,37	16,53	1,03 1,13	1,07	15,84 15,20	15,69

Note: Solvent — butyl alcohol, reaction temperature 117°.

The action of alkali led to the decomposition of the complex with the formation of the original nitroaromatic compound, mercuric oxide and the corresponding salt of trinitromethane, for example:

$$NO_2C_6H_3 \cdot Hg[C(NO_2)_3]_2 + 2KOH \rightarrow NO_2C_6H_5 + HgO + 2KC(NO_2)_3 + H_2O.$$

The mercury salt of trinitromethane did not react with m-dinitrotoluene, m-dinitroanisole and m-trinitrobenzene, i.e. with compounds containing substituents in the positions meta to the nitro group. This observation indicates the following structure for the complex:



We also studied the action of the mercury salt of trinitromethane on compounds containing a double bond. As is known [3], in a solvent of the general formula ROH, a series of mercury salts add to olefins with the formation of β-mercurated alcohols or ethers by the scheme:

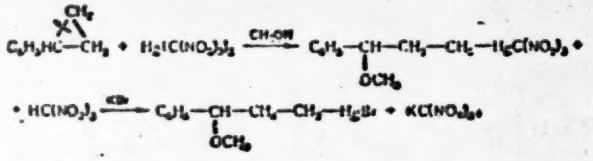
$$HgX_2 + ROH \rightleftarrows RO-HgX + HX$$

$$ROHgX + C=C \rightleftarrows -\underset{OR}{C}-\underset{HgX}{C}- \qquad (I)$$

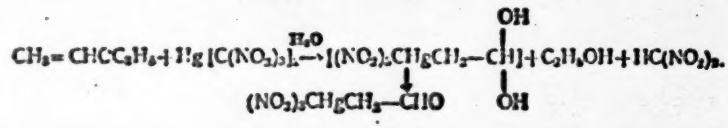
By studying the reaction of $Hg[C(NO_2)_3]_2$ with ethylene in water or alcohol solutions, we established that the reaction products were not the expected alcohol or ether, but trinitromethyl-3,3,3-trinitropropylmercury:

$$H_2C=CH_2 + Hg[C(NO_2)_3]_2 \rightarrow (NO_2)_3CCH_2CH_2HgC(NO_2)_3. \qquad (II)$$

The same compound was also formed in the reaction of the mercury salt of trinitromethane with ethylene in nitrobenzene and nitromethane. This may be considered as proof that the formation of trinitromethyl-3,3,3-trinitropropylmercury proceeds by the direct addition of the elements of the mercury salt of trinitromethane to ethylene [Scheme (I)]. We should emphasize that this type of addition of mercury salts to a double bond is a new reaction in the chemistry of organomercury compounds. However, in studying the reaction of the mercury salt of trinitromethane with phenylcyclopropane and vinyl ethyl ether in aqueous or alcoholic media, we showed that this salt was able to react in the form of its hydr(alk)oxide, i. e. by Scheme (I) with the formation, in the case of phenylcyclopropane, of the γ-mercurated ether, which reacted with potassium bromide to give 3-methoxy-3-phenylpropylmercuric bromide, that is described in the literature [4]:



and vinyl ethyl ether gave trinitromethylmercuracetaldehyde (by the general reaction scheme for vinyl ethers with mercury salts [5]):



It is interesting to note that not only the mercury salt of trinitromethane itself, but also a compound of the type $R-HgC(NO_2)_3$ is capable of adding to a double bond. Thus, for example, chloromercuritrinitromethane

(formed by the reaction of trinitromethane with an aqueous solution of mercuric chloride) reacts with ethylene to give trinitropropylmercury chloride:

$$(NO_2)_3CHgCl + CH_2=CH_2 \rightarrow (NO_2)_3CCH_2CH_2HgCl,$$

and trinitromethyl-3,3,3-trinitropropylmercury gives bis-trinitropropylmercury:•

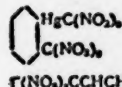
$$(NO_2)_3CCH_2CH_2HgC(NO_2)_3 + CH_2=CH_2 \rightarrow [(NO_2)_3CCH_2CH_2]_2Hg.$$

The addition of the mercury salt of trinitromethane to a double bond was studied on the examples of propylene, styrene, cyclohexane, allyl alcohol and methyl acrylate. In all cases, the reaction proceeded by Scheme (II). The mercury salt of trinitromethane reacted with allyl alcohol immediately, even in aqueous solution, by the equation:

$$2CH_2=CHCH_2OH + Hg[C(NO_2)_3]_2 \rightarrow [(NO_2)_3CCHCH_2]_2Hg$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2OH$$

Table 3 gives the constants and yields of some of the substances obtained.

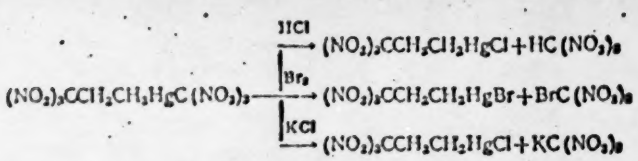
TABLE 3

Formula	M.p., °C	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$(NO_2)_3CCH_2CH_2HgC(NO_2)_3$	167	93	8.97 9.13	9.09	0.79 0.82	0.76	15.96 15.97	15.99
$(NO_2)_3CCH_2CH_2HgCl$•	142	92	—	—	—	—	—	—
$[(NO_2)_3CCH_2CH_2]_2Hg$	155	84	12.73 12.86	12.94	1.46 1.49	1.45	14.82 15.06	15.09
$(NO_2)_2CCHCH_2HgC(NO_2)_3$ CH_3	134	97	11.04 11.16	11.06	1.17 1.21	1.11	—	—
$[(NO_2)_2CCHCH_2]_2Hg$ CH_3	124	79	16.62 16.69	16.42	2.19 2.23	2.06	14.15 14.21	14.28
$(NO_2)_2CCHCH_2HgC(NO_2)_3$ C_6H_5	129	80	19.53 19.72	19.85	1.38 1.43	1.33	—	—
	95	55	16.47 16.53	16.48	1.70 1.81	1.73	—	—
$[(NO_2)_2CCHCH_2]_2Hg$ CH_2OH	109	70	15.57 15.71	15.58	2.07 2.10	1.96	13.71 13.89	13.62
$(NO_2)_2CCH_2CH-HgC(NO_2)_3$ $COOCH_3$	150	82	12.26 12.28	12.28	0.93 1.22	1.03	—	—
$(NO_2)_2CH_2CH_2CHO$	128	65	9.22 9.31	9.15	0.78 0.84	10.76	10.71 10.02	10.67

• Found %: Cl 8.65; 8.73. Calculated %: Cl 8.58.

While the symmetrical organomercury polynitro compounds are quite stable to the action of acids, halogens and halide salts, the unsymmetrical ones react with them by the scheme:

• Bis-trinitropropylmercury may be obtained directly from the mercury salt of trinitromethane and ethylene by performing the reaction in an alcohol medium, without isolating the trinitromethyltrinitropropylmercury.



The mercury salt of trinitromethane does not add to olefins of iso-structure (iso-butylene and 3-ethylpentene-3), even though they only have one quaternary carbon atom at the double bond.

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FLUOROSILICOORGANIC COMPOUNDS

A STUDY OF THE ADDITION OF ALKYLCHLOROSILICON HYDRIDES TO 1,1,2,2-TETRAFLUOROETHYL ALLYL ETHER

Corresponding Member of the Academy of Sciences USSR
A. D. Petrov, V. A. Ponomarenko, G. V. Odabashyan and
S. I. Krokhmalev

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

In previous work [1] we showed that the addition of alkylchlorosilicon hydrides to 1,1,2-trifluoro-2-chloroethyl allyl ether ($CH_2=CHCH_2OCF_2CF(Cl)H$) (A) in the presence of platinized charcoal was a convenient method synthesizing simple fluorosilicoorganic ethers. On the basis of data on the combined addition to $CH_2=CHCH_2OCF_2CF(Cl)H$ of appropriate pairs of alkylchlorosilicon hydrides, the latter were arranged (according to the relative yields of the addition products) in the following series:

$$(CH_3)(C_2H_5)_2SiH > (CH_3)(C_2H_5)(Cl)SiH > (C_2H_5)(Cl)_2SiH > Cl_3SiH$$

in contrast to the addition of the same alkylsilicon hydrides in the absence of a "competing" silicon hydride.*

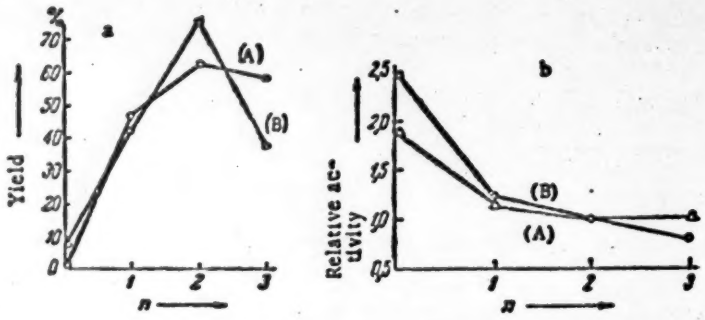

Fig. 1. The addition of alkylchlorosilicon hydrides $(CH_3)(C_2H_5)_2SiH$, $(CH_3)(C_2H_5)(Cl)SiH$, $(C_2H_5)(Cl_2)SiH$ and Cl_3SiH to (A) and (B): a) yield of addition products, b) relative activity of alkylchlorosilicon hydrides, determined by the "competition" method. n is the number of Si – Cl bonds in $R_3(Cl)SiH$.

In this work we investigated this reaction in more detail on the example of the same alkylchlorosilicon hydrides and 1,1,2,2-tetrafluoroethyl allyl ether, $CH_2=CH\cdot CH_2OCF_2CF_2H$ (B). All the experiments were performed under similar conditions (see Tables 1 and 2). The results thus obtained completely confirmed the conclusions presented above (see Fig. 1).

* In this case, $C_2H_5SiHCl_2$ and $(CH_3)(C_2H_5)(Cl)SiH$ add most readily and $(CH_3)(C_2H_5)_2SiH$ with the greatest difficulty.

In the addition of $(CH_3)(C_2H_5)_2SiH$ to (B), neither drying the catalyst in vacuum (2 mm) at 300°, nor treating it with C_2H_5OH, nor performing the reaction in the presence of $(CH_3)_2SiCl_2$ to remove possible moisture led to an increase in the yield of addition product. However, the addition of even small amounts of $C_2H_5SiHCl_2$ sharply increased the yield of addition products.• This fact and all those noted above indicate the following: 1) the addition of silicon hydrides on platinized charcoal is possibly a radical chain reaction; 2) an essential role is apparently played in this process by the absorption forces of the reacting molecules on the catalyst surface; 3) the ease of formation and activity of the silyl radicals depends on the character of the substituents at the Si; activity differences in the silyl radicals (together with other factors) may explain the peculiarities of the addition reaction noted above.

$$\equiv Si-H + R_F^{\bullet\bullet} \rightarrow \equiv Si^{\bullet} - R_F$$

TABLE 1

Expt. no.	Starting hydrides ••	Total hydride, g (mole)	R_F, g (mole)	Max. react. temp. °C	Max. pressure, atm.	Reaction products	Yield g	Yield %
1	Cl_3Si-H	40.6 (0.3)	47.5 (0.3)	161	11	Cl_3Si-R_F	51	58.0
2	$(CH_3)(Cl)_2SiH$•••	34.5 (0.3)	47.5 (0.3)	162	11	$(CH_3)(Cl)_2SiR_F$	29	35.0
3	$(C_2H_5)(Cl)_2SiH$	38.7 (0.3)	47.5 (0.3)	160	10	$(C_2H_5)(Cl)_2SiR_F$	54	63.0
4	$(C_2H_5)(Cl)_2SiH$	36 (0.25)	40 (0.25)	163	8	$(C_2H_5)(Cl)_2SiR_F$	30	40.0
5	$(CH_3)(C_2H_5)(Cl)SiH$	32.6 (0.3)	47.5 (0.3)	160	11	$(CH_3)(C_2H_5)(Cl)SiR_F$	37	46.0
6	$(CH_3)(C_2H_5)_2SiH$••••	29.7 (0.3)	47.5 (0.3)	172	16	$(CH_3)(C_2H_5)_2SiR_F$	traces	—

• $R_F = CH_2 = CHCH_2OCF_2CF_2H$.

•• All reactions were performed in the presence of 0.3 g of 1% Pt/C 0.3 parts, reaction time, 3 hours.

••• The low yield of addition product was apparently connected with the impurity of the CH_3SiCl_2H.

•••• A reaction with 0.2 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol at room temperature gave 22 g of addition product (28.1%) after 30 minutes.

TABLE 2

Expt. no	Starting hydrides•	Max. react. temp. °C	Max. pressure, atm.	Addition products	Yield g	Yield %
1	$C_2H_5SiHCl_2$	167	11.5	$C_2H_5(Cl)_2SiCH_2CH_2CH_2OCF_2CF_2H$	30.2	35
	Cl_3SiH			$Cl_3SiCH_2CH_2CH_2OCF_2CF_2H$	28.4	32
2	$C_2H_5SiCl_2H$	170	8	$(C_2H_5)(Cl)_2SiCH_2CH_2CH_2OCF_2CF_2H$	25.0	29
	$(CH_3)(C_2H_5)SiClH$			$(CH_3)(C_2H_5)(Cl)SiCH_2CH_2CH_2OCF_2CF_2H$	29.4	35
3	$C_2H_5SiCl_2H$	158	7	$(C_2H_5)(Cl)_2SiCH_2CH_2CH_2OCF_2CF_2H$	17.0	20
	$(CH_3)(C_2H_5)_2SiH$			$(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2OCF_2CF_2H$	17.3	19
4	Cl_3SiH	172	12	$Cl_3SiCH_2CH_2CH_2OCF_2CF_2H$	28.4	19
	$(CH_3)(C_2H_5)_2SiH$			$(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2OCF_2CF_2H$	20.0	25

• For the reaction we used 0.3 mole of each hydride and 0.3 mole of $CH_2=CH-CH_2OCF_2CF_2H$. The amount of catalyst (1% Pt/C) was 0.3 g. The reaction time was 3 hours.

• The addition of $(CH_3)(C_2H_5)_2SiH$ to (B) in the presence of $H_2PtCl_6 \cdot 6H_2O$ began at room temperature and proceeded at a high rate.

The structure of the addition products was proved by synthesis by the scheme:

$$Cl_3SiH+CH_2=CHCH_2OCF_2CF_2H \xrightarrow{CH_3MgBr} (CH_3)_2SiCH_2CH_2CH_2OCF_2CF_2H \quad (1)$$

$$(CH_3)_2SiCH_2CH_2CH_2OH+CF_2=CF_2 \xrightarrow{Na} (CH_3)_2SiCH_2CH_2CH_2OCF_2CF_2H \quad (2)$$

Comparison of the Raman spectra of the two compounds and also their other physical properties indicated that they were identical.

In conclusion, we should note that the fluoroethers of the γ-hydroxypropyltrialkylsilanes obtained did not give the corresponding esters when treated with 96% H_2SO_4 at 0-10° according to the scheme:

$$R_3SiCH_2CH_2CH_2OCF_2CF_2H+H_2O \xrightarrow[0-10^\circ]{H_2SO_4} R_3SiCH_2CH_2CH_2OCOCF_2H+2HF$$

As known [2], a similar reaction proceeds very readily under these conditions with ethers of the type $ROCF_2CF_2I$ (R = CH_3, C_2H_5, C_3H_7, etc.).

1. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropyltrichlorosilane $Cl_3SiCH_2CH_2CH_2OCF_2CF_2H$ (I). 40.6 g (0.3 mole) of trichlorosilane and 47.5 g (0.3 mole) of (B) were heated at 161° in the presence of 0.3 g of 1% platinum on charcoal for 3 hours in a stainless steel autoclave of 200 ml capacity. The maximum pressure was 11 atm. The weight of reaction products was 81.5 g. Distillation of them on a column with glass packing yielded 51 g (58%) of pure (I) with b.p. 186°/751 mm, d^{20}_4 1.4335, $n^{20}D$ 1.3994, MR found 49.58, calculated 49.58.

Found %: C 20.54; 20.51; H 2.46; 2.57; Cl 36.18; 36.23; F 24.77; 24.53 $C_5H_7SiCl_3F_4O$.
Calculated %: C 20.46; H 2.40; Cl 36.23; F 25.89

2. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropylmethyldichlorosilane, $(CH_3)(Cl)_2SiCH_2CH_2CH_2OCF_2CF_2H$ (II). The reaction conditions are given in Table 1. The weight of reaction products was 75.5 g. Distillation as in Experiment 1 yielded 29 g (35%) of pure (II) with b.p. 190.1°/750 mm, d^{20}_4 1.5140, $n^{20}D$ 1.3960; MR found 49.95, calculated 49.96.

Found %: C 26.69; 26.62; H 3.73; 3.53; Cl 26.29; 26.03; F 26.15; 26.53 $C_6H_{10}SiCl_2F_4O$.
Calculated %: C 26.38; H 3.69; Cl 25.97; F 27.82

3. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropylethyldichlorosilane, $(C_2H_5)(Cl)_2SiCH_2CH_2CH_2OCF_2CF_2H$ (III). The reaction conditions are given in Table 1. The weight of reaction products was 80 g. Distillation as in experiment 1 yielded 54 g (63%) of pure (III) with b.p. 207.2°/749 mm, d^{20}_4 1.2837; $n^{20}D$ 1.4033; MR found 54.63, calculated 54.46.

Found %: C 29.54; 29.43; H 4.24; 4.36; Cl 25.49; 25.78; F 25.33; 24.71 $C_7H_{12}SiCl_2F_4O$.
Calculated %: C 29.28; H 4.21; Cl 24.70; F 26.46

4. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropylpropyldichlorosilane, $(C_3H_7)Cl)_2SiCH_2CH_2CH_2OCF_2CF_2H$ (IV). See Table 1 for the reaction conditions. The weight of reaction products was 70 g. Distillation in vacuum yielded 30 g (40%) of pure (IV) with b.p. 101°/11 mm, d^{20}_4 1.2484, $n^{20}D$ 1.4062; MR found 59.29, calculated 59.21.

Found %: Cl 23.51; 23.66; F 24.77; 25.05 $C_8H_{14}SiCl_2F_4O$. Calculated %: Cl 23.54; F 25.23

5. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropylmethylethylchlorosilane, $(CH_3)(C_2H_5)(Cl)SiCH_2CH_2CH_2OCF_2CF_2H$ (V). The reaction conditions are given in Table 1. The weight of reaction products was 75 g. Distillation as in Experiment 1 yielded 37 g (45%) of pure (V) with b.p. 199.0°/749 mm, d^{20}_4 1.1681, $n^{20}D$ 1.3956; MR found 54.82, calculated 54.83.

Found %: Cl 14.30; 14.01; F 27.22; 27.14 $C_8H_{15}SiClF_4O$. Calculated %: Cl 13.29; F 23.49

6. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropylmethyldiethylsilane, $(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2OCF_2CF_2H$ (VI). To 30.7 g (0.3 mole) of methyldiethylsilane and 47.5 g (0.3 mole) of (B) was added 0.2 ml of 0.1 M $H_2P+Cl_6 \cdot 6H_2O$ in isopropyl alcohol. The reaction began vigorously at room temperature with strong evolution

of heat and the precipitation of a black precipitate. The flask was cooled with water. The reaction proceeded for 30 minutes. The weight of reaction product was 64 g. Distillation as in Experiment 1 gave 22 g (28%) of pure (VI)* with b.p. 196.5°/749 mm, d^{20}_4 1.9422, $n^{20}D$ 1.3930; MR found 59.62, calculated 59.47.

7. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropyltrimethylsilane, $(CH_3)_3SiCH_2CH_2CH_2OCF_2CF_2H$ (VII). To the Grignard reagent prepared from 13.2 g (0.54 g-at) of Mg in 150 ml of abs. ether and CH_3Br, 44 g (0.15 mole) of (I) was added dropwise with vigorous stirring. The reaction mixture was heated for 4 hours under reflux with stirring. After treatment with water, the ether layer was separated and dried over $CaCl_2$, together with the ether extract. Distillation as in Experiment 1 yielded 20.4 g (58.9%) of pure (VII) with b.p. 156°/746 mm, d^{20}_4 1.0453, $n^{20}D$ 1.3732; MR found 50.66, calculated 50.69.

8. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropyldimethylethylsilane, $(CH_3)(C_2H_5)SiCH_2CH_2CH_2OCF_2$·$CF_2$ (VII). 43.1 g (0.15 mole) of (III) was added drop wise with vigorous stirring to the Grignard reagent prepared from 8.8 g (0.36 g-at) of Mg in 120 ml of abs. ether and CH_3Br. The reaction mixture was heated for 4 hours under reflux with stirring. After treatment with water, the ether layer was separated and dried over Na_2CO_3 with the ether extract. Distillation as in Experiment 1 yielded 25.0 g (67.5%) of pure (VIII) with b.p. 176°/739 mm, d^{20}_4 1.0402, $n^{20}D$ 1.3830; MR found 55.24, calculated 55.20.

9. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropyldimethylpropylsilane, $(CH_3)_2(C_3H_7)SiCH_2CH_2CH_2O$·$CF_2CF_2H$ (IX). 23 g (0.073 mole) of (IV) was added dropwise with vigorous stirring to the Grignard reagent prepared from 4 g (0.16 g-at) of Mg in 100 ml of abs. ether and CH_3Br. The reaction mixture was heated for 2 hours under reflux with stirring After treatment with water, the ether layer was separated and dried over Na_2SO_4 together with the ether extract. Distillation as in Experiment 1 yielded 11 g (57.3%) of pure (IX) with b.p. 193°/751 mm, d^{20}_4 1.0267, $n^{20}D$ 1.3886; MR found 59.92, calculated 59.95.

10. 1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropyltrimethylsilane, $(CH_3)_3SiCH_2CH_2CH_2OCF_2CF_2H$ (VII). 0.4 g (0.017 g-at) of Na was dissolved in 21 g (0.16 mole) of γ-hydroxypropyltrimethylsilane. The reaction mixture was placed in a stainless steel autoclave with a capacity of 200 ml. $CF_2=CF_2$ was passed into the autoclave from a tank at 10 atm. pressure as it was absorbed at room temperature. The autoclave was shaken periodically. The saturated reaction product was removed from the autoclave, washed with water, dried over Na_2SO_4 and distilled on a column with a glass packing. We obtained 18 g (48.7%) of pure (VII) with b.p. 156°/746 mm, d^{20}_4 1.0428, $n^{20}D$ 1.3732; MR found 50.78, calculated 50.68.

11. 1,1,2,2-Tetrafluoroethyl ether of β-hydroxyethyltrimethylsilane, $(CH_3)_3SiCH_2CH_2OCF_2CF_2H$ (X). 0.53 g (0.023 g-at) of Na was dissolved in 25 g (0.21 mole) of β-hydroxyethyltrimethylsilane. The reaction was performed under the condition of Experiment No. 10. After distillation of the reaction products on a column with a glass packing, we obtained 10 g (21.6%) of pure (X) with b.p. 137°/746 mm, d^{20}_4 1.0427, $n^{20}D$ 1.3732; MR found 50.78, calculated 50.69.

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* The conditions presented in Table 1, with the use of 1% Pt/C, yielded mainly an azeotropic mixture of the starting materials (b.p. 69°) and only traces of the additional product. When 1 g of $C_2H_4SiCl_2H$ and 0.3 g of 1% Pt on charcoal was added to 25 g of this azeotropic mixture under the same conditions, distillation yielded 7.3 g (38%) of pure (VI) with b.p. 195.8°/739 mm d^{20}_4 1.0412; $n^{20}D$ 1.3926.

•• Original Russian pagination. See C. B. Translation.

CHANGES IN THE CHEMICAL COMPOSITION AND ACTIVITY OF COPPER CATALYSTS DURING THE OXIDATION OF PROPYLENE TO ACROLEIN

N. I. Popova and E. E. Vermel'

East Siberian Branch of the Academy of Sciences USSR

(Presented by Academician B. A. Kazanskii, October 3, 1958)

In the study of oxidation reactions, a change in the chemical composition of the catalyst during the reaction is often observed. G. K. Boreskov [1] developed the idea that the change in the chemical and physical properties and, consequently, in the activity of the catalysts under the effect of the reaction system was of a general character. He considered that as a result of this process, a certain stationary composition of the catalyst was established and this was determined by the ratio of the rates of combining or consumption of a particular component of the catalyst as a result of interaction with the reacting substances. However, chemical conversions of catalysts under the action of the reacting substances are mainly observed only in the study of catalytic oxidation processes on oxide catalysts (V_2O_5, CuO, Cu_2O). The relation between the chemical conversions of copper catalysts during the reaction and their activity has been studied very little.

V. A. Komarov and N. S. Burevovaya [2] investigated the change in chemical composition of a catalyst consisting of cuprous and cupric oxide, during the oxidation of isopropyl alcohol. The authors showed that during the reaction the catalyst was reduced to copper (with traces of cuprous oxide), whereupon its activity fell slightly.

O. V. Isaev, M. Ya. Kushnerov and L. Ya. Margolis [3] studied phase changes of copper catalysts during the oxidation of propylene with air, using x-ray and electronographic ana'ysis. It was established that, regardless of the original composition (pure CuO, Cu_2O or Cu), the phase composition of the catalyst changed to the system Cu_2O + Cu or CuO + Cu_2O + Cu. The authors proposed that the activity of the catalyst depended on the degree of its reduction to cuprous oxide and copper. However, no experimental data confirming this premise was presented in the work.

The authors of the present work and R. N. Strukova [4] showed that the stability and activity of a copper oxide catalyst during the oxidation of propylene depended strongly on the composition of the mixture of gases oxidized.

It was interesting to determine to what extent this phenomenon was connected with chemical conversions of the catalyst under the effect of the reacting gases.

We should note that x-ray and electronographic methods make it possible to investigate a change in the chemical composition of copper catalysts only qualitatively and then only for catalysts with a high cupric oxide content on the carriers. Meanwhile, N. I. Popova, V. I. Belyaev and R. N. Stukova [5] showed that such catalysts had a low activity in the oxidation of propylene into acrolein. Under these conditions, the most active catalysts were those containing 1-1.5% cupric oxide on silicon carbide. Due to this, it seemed interesting to study the chemical conversions of catalysts with different cupric oxide contents on the carrier using chemical methods, making it possible to follow not only qualitative, but also quantitative changes in the chemical composition of the catalysts.

For this purpose we used procedures described in the literature [3,5,6] to prepare catalysts containing CuO,

Cu_2O and Cu, deposited on silicon carbide in concentrations corresponding to cupric oxide amounts of 1.5, 3.0 and 5.0 weight %. The propylene was oxidized in a glass U-shaped reactor by the procedure described in our previous communications [4, 5]. The temperature in the reaction zone was kept at 368-370° and since the catalyst bed was small (30 mm), the fall in temperature along the catalyst bed did not exceed 2-3°. The contact time was 2 sec. in all experiments. The reaction was continued for an hour and then the catalyst tube was

TABLE 1

Change in the Chemical Composition of Copper catalysts during the Oxidation of Propylene

Expt. no.	Volume ratio C_3H_6 : O_2	Concentration of copper on silicon carbide (calculated on CuO in weight %)	Composition of catalyst (calculated on copper in weight %)						Amount of propylene converted / hour / liter of catalyst (moles)		
			before expt.			after expt.					
			CuO	Cu_2O	Cu	CuO	Cu_2O	Cu	into carbonyl c'mp'ds	into acrolein	into CO_2
1	7.5 : 1	1.5	4.6	4.6	90.8	74.3	22.9	2.8	1.7	—	—
2	7.5 : 1	1.5	0.0	100.0	0.0	69.5	30.5	0.0	1.8	1.0	0.6
3	7.5 : 1	1.5	93.7	6.3	0.0	69.8	30.2	0.0	—	—	—
4*	7.5 : 1	1.5	0.0	100.0	0.0	78.0	21.5	0.5	2.6	2.0	0.5
5	4.0 : 1	1.5	58.3	22.7	18.0	73.2	26.8	0.0	2.4	—	—
6	4.0 : 1	1.5	0.0	100.0	0.0	67.5	32.5	0.0	2.2	1.0	2.0
7	30.0 : 1	1.5	0.0	100.0	0.0	73.6	26.4	0.0	1.4	—	0.1
8	30 : 1	3.0	0.0	100.0	0.0	70.1	5.4	24.5	1.0	—	—
9	30 : 1	5.0	0.0	100.0	0.0	49.0	12.2	38.8	0.3	—	0.3
10	30 : 1	1.5+3.5% Ag	0.0	100.0	0.0	—	—	—	0.5	0.25	—
11	7.5 : 1	5.0	0.0	100.0	0.0	65.5	9.2	25.3	1.2	—	1.3
12	7.5 : 1	1.5+3.5% Ag	0.0	100.0	0.0	—	—	—	1.5	0.31	—
13	7.5 : 1	1.5 (on Al_2O_3)	0.0	100.0	0.0	—	—	—	0.1	—	1.4
14	7.5 : 1	1.5+1% Al_2O_3 (on silicon carbide)	0.0	100.0	0.0	—	—	—	0.7	—	1.3

* In experiment No. 4 the time of catalytic action was 8 hours.

cooled with a stream of nitrogen (containing 0.02% oxygen by volume) and the catalyst analyzed for CuO, Cu_2O and Cu by N. A. Tananaev's method [7]. The acrolein was determined by the bromide-bromate method. The chemical composition of the catalyst was expressed in weight percents of monovalent, divalent and metallic copper relative to the total amount of copper on the carrier.

The results of the experiments are given in Table 1. As this shows, for catalysts where the concentration of copper corresponds to 1.5% CuO on the silicon carbide, regardless of the original phase composition, a similar chemical composition (about 70% Cu_2O and about 30% CuO) is established after an hour as a result of the interaction of the system catalyst – propylene – oxygen.

It is interesting that the ratio of the cuprous and cupric oxides depends comparatively little on the composition of the reacting gas mixture for this catalyst. As Table 1 shows, together with this, the amount of propylene converted to carbonyl compounds on the catalyst over an hour is different in all experiments and depends strongly on the composition of the starting gas mixture. At the same time, the amounts of acrolein, obtained on the catalyst over the same time and under the same conditions, were similar. Apparently, this may be explained by the fact that the formation of carbonyl compounds other than acrolein occurs mainly on cupric oxide and, possibly, partly in the space. In addition, besides the formation of carbonyl compounds, the propylene may be oxidized to CO_2 and H_2O on the catalyst. Therefore in this case there is no correlation between the change in the chemical composition of the catalyst under the action of the reacting gases and its activity. On the other hand, the composition of the reacting gas mixture has a very strong effect on the stability of the catalyst (see Fig. 1). With a propylene to oxygen ratio of 7.5 : 1 in the mixture, as the time of catalytic action increases (see Table 1, Exp.

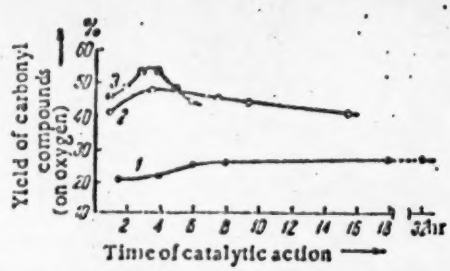

Fig. 1. Relation of activity of copper catalysts to time of catalytic action. See Table for conditions: Exp. No. 2 for Curve 1, Exp. No. 7 for Curve 2 and Exp. No. 8 for Curve 3

No. 4) during the first 8-10 hours, the cuprous oxide content of the catalyst increases (possibly due to conversion of cupric oxide into cuprous oxide, not only on the surface of the catalyst granules, but also inside them) and there is a corresponding increase in the amount of propylene converted into carbonyl compounds and especially into acrolein. After this, the catalyst operates stably for a long time (see Fig. 1, 1).

In the case of oxidation of a mixture containing a small amount of oxygen (a ratio of propylene to oxygen of 30:1), the reduction of the catalyst goes more rapidly and the catalyst operates less stably, possibly due to further gradual conversion of the cuprous oxide into copper (see Fig. 1, 2).

The composition of the catalyst after experiments depends not only on the time of catalytic action, but, as Table 1 shows (see Expt. No. 7-9 and 11), also on the concentration of the copper oxides on the carrier and also on the nature of the carrier (see Exps. No.10 and 12-14). The catalysts with a 3-5% cupric oxide content on silicon carbide change their chemical composition to the system $CuO + Cu_2O + Cu$ in the interaction with the reaction medium. The appearance of metallic copper in the catalyst sharply decreases the yield of carbonyl compounds. The introduction of silver or aluminum oxide into the catalyst has a similar effect on the activity of the catalyst. Due to the rapid reduction of cuprous oxide to copper, the composition of the reacting gases has a particularly marked effect on catalysts with high concentration of cupric oxide on silicon carbide (see Fig. 1, 3). This phenomenon is also connected with deactivation of a copper catalyst during the oxidation of propylene containing a trace of isopropyl alcohol, since, according to the data of V. A. Komarov and N. S. Burevovaya [2], in the oxidation of isopropyl alcohol on copper oxide catalysts, the latter are reduced to copper.

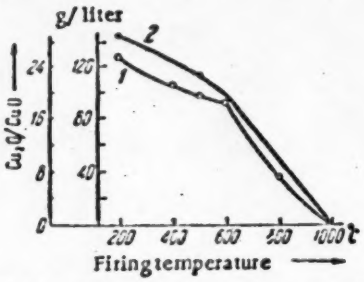

Fig. 2. Effect of firing temperature of catalyst on its properties.
1) Change in catalyst activity;
2) change in chemical composition (see Table, Expt. No. 2 for conditions).

The second reason for deactivation of the catalysts is agglomeration of the copper oxide. It then loses its capacity for reduction to cuprous oxide. This phenomenon was observed in an investigation of the activity of copper oxide catalysts on carriers, fired at different temperatures (see Fig. 2). Therefore superheated places in the catalyst should be avoided.

The third reason for deactivation of the catalysts studied is, apparently, the polymerization of acrolein on its surface. The activity of the catalysts is readily restored by passing mixtures rich in oxygen over them as in this case, metallic copper is readily oxidized to CuO and the polymers are burned.

Thus, the activity and stability of a copper catalyst depends to a considerable degree on the change in its chemical composition, occurring during the interaction of the catalyst with the reaction medium.

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INVESTIGATION OF WEIGHABLE AMOUNTS OF TECHNETIUM

Academician V. I. Spitsyn and A. F. Kuzina

Institute of Physical Chemistry, Academy of Sciences, USSR

This work was devoted to the preparation of chemically pure technetium compounds – its heptasulfide and ammonium pertechnate. An examination was made of the absorption spectra of the pertechnate ion, a gravimetric analysis was performed on the heptasulfide and the absolute activity of the technetium preparation isolated was measured.

The starting material used for the extraction of technetium was molybdenum trioxide, irradiated for a long time with thermal neutrons, whose flux was $2.5 \cdot 10^{13}/\text{cm}^2 \cdot \text{sec}$. The technetium was isolated from an ammonium molybdate solution by adsorption on sparingly soluble crystalline precipitates of magnesium ammonium phosphate and magnesium hydrophosphate [1]. The subsequent extraction of technetium was based on the fact that in the reduced state, technetium is not absorbed by phosphate precipitates. The magnesium ammonium phosphate was dissolved in 6 N HCl and hydrogen sulfide passed into the solution for a long time. This reduced the technetium to the tetravalent and partly to the divalent state. NH_4OH was added to the solution. The precipitate of magnesium phosphate formed did not take out technetium. Evaporation of the solution to dryness and heating removed volatile chlorides. The residue, containing technetium was dissolved in nitric acid and passed through a chromatography column with the cationite KU-2 at pH 2. The technetium was collected in the filtrate in an anionic form.

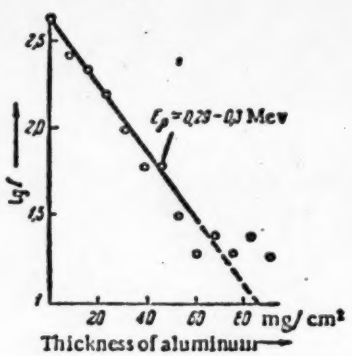

Fig. 1. Absorption curve of technetium radiation by aluminum.

We should note that the heptasulfide is an important compound in the normal purification scheme of technetium. It is the main standard in analyses and determining the half-life of technetium. Therefore, in our work the concentration of technetium ended with the isolation of the heptasulfide.

The filtrate was evaporated after the chromatographic operation. The residue was a white, slightly pink, friable powder, consisting mainly of ammonium nitrate and a compound of reduced technetium. Its weight was 56 mg. The ammonium nitrate was removed by heating the preparation to 160° in a silica boat in a tubular electrical microfurnace. The residue was treated with the minimal amount (2-3 drops) of hydrogen peroxide and ammonia, dried at 40-50° and weighed. The weight at this stage was 14 mg. This residue was dissolved in 4 N HCl and the liquid filtered through a glass microfilter. The volume of filtrate obtained was 4 ml. Measurement of the absolute activity of this solution (see below) gave a value corresponding to 0.918 mg of technetium. A stream of hydrogen sulfide was passed through this solution. The black-brown precipitate formed was centrifuged using a hand microcentrifuge, into which were placed special tubes measuring 4 x 15 mm. The centrifuged precipitate was transferred to a silica microextractor, where the technetium sulfide was extracted with carbon disulfide in 1 ml portions and collected in a receiver. The carbon disulfide was then removed by evaporation in air and the preparation dried at 110°.

The purified technetium sulfide collected was examined for the presence of radiochemical impurities by absorption of the radiation in aluminum. As the absorption curve (Fig. 1) shows, radiochemical impurities were

absent and the energy of the radiation of the preparation agreed with literature data [2]. The weight of the preparation was 2.987 mg. The bulk of the preparation obtained was used for its gravimetric analysis and only a small portion of the order of 0.05 mg was required for spectrophotometric analysis and approximately 0.36 mg for measurement of the absolute activity of the preparation.

TABLE 1

Analysis of Technetium Heptasulfide

Sample no.	Wt., mg	$BaSO_4$ obtained, mg	S found		Tc calc. (by difference)	
			mg	%	mg	%
1	0.679	2.973	0.407	59.94	0.272	40.06
2	0.639	2.392	0.315	49.28	0.324	50.72
3	0.966	3.754	0.514	53.21	0.452	46.79
Total	2.284		1.236		1.048	
Average				54.14		45.86
Calc. for Tc_2S_7				53.13		46.87

The technetium heptasulfide was analyzed gravimetrically by the method described in [3]. The procedure for work with small amounts of substances was used.

The purified preparation of technetium sulfide was treated with the minimal amount of hydrogen peroxide and ammonia and carefully dried at 40-50°, after which it was dissolved in 6 ml of 0.1 N HCl. The total solution was divided into three samples, for which the weight of the technetium sulfide was 0.679, 0.639 and 0.966 mg. The solution of each of these samples, diluted to 5 ml, was heated on a microburner and 1% $BaCl_2$ solution added to it (during precipitation, the reaction solution was heated on a water bath). The precipitate of $BaSO_4$ was filtered with a platinum Gooch microcrucible, washed with hot water with a drop of sulfuric acid and then again with water. The dried, fired $BaSO_4$ precipitate was weighed on a VM-20 microbalance. Then the sulfur content of each sample was calculated in the usual way and from the sulfur content, the technetium content. The analysis results are given in Table 1.

The gravimetric analysis of technetium heptasulfide was checked by comparing it with the results of radiometric analysis. The weight of technetium was determined by direct measurement of the absolute activity of the preparation. This measurement was performed in parallel with the gravimetric analysis.

The absolute activity of the technetium preparation isolated was calculated by the usual formula

$$a = \frac{I}{3.71 \cdot 10^4 \cdot 60 pkqs\omega}\ \mu C,$$

where a is the absolute activity of the preparation in microcuries, I, the observed activity in counts per minute; p, the number of β-particles emitted per disintegration act; k, the coefficient allowing for the absorption of β-particles in the walls of the counter and the air layer; s, the coefficient allowing for the absorption of β-particles in the preparation; q, the back-scattering coefficient; ω, the geometry correction, which is calculated by the formula $\omega = 0.5(1 - \cos\alpha)$, $\cos\alpha = h/(h^2+r^2)^{\frac{1}{2}}$; h, the distance from the preparation to the counter wire and r the radius of the counter window.

The measurements were carried out with an end-window counter with a mica window 1.8 mg/cm² thick. The preparation, mounted on a thin plexiglas film, whose thickness was measured in tenths of a micron, was placed at a distance of 1 cm from the counter wire. The counter holder was made of plexiglas to decrease the reflection of β-particles. The coefficients q and s, measured under these conditions, equalled 1. The diameter of the sample measured was half the radius of the counter window, i.e. 0.5 cm. Hence $\cos\alpha = h/(h^2+r^2)^{\frac{1}{2}} = 0.7$; $\omega = 0.5(1-\cos\alpha) = 0.15$. The coefficient p = 1 and the coefficient k = 0.7. The observed activity I was $0.37 \cdot 10^6$ counts/min. On the basis of these data, the total absolute activity of the three technetium samples taken for gravimetric analysis (see Table 1) was $a = 0.37 \cdot 10^6/3.71 \cdot 10^4 \cdot 60 \cdot 0.7 \cdot 0.15 = 15.3\ \mu C$, which corresponds to 0.918 mg of metallic technetium, taking its specific activity as equal to 20 μC/mg.

The deviation of the results of the radiometric and gravimetric analyses was 5.4%.

Ammonium pertechnate was examined spectrophotometrically on an SF-4 spectrophotometer. Prismatic silica cells, 1 cm long, were used. The absorption spectra of the solution were studied in the wavelength range 2100-2300 A at intervals of 50A with various slit widths from 0.333 to 0.092 mm at constant sensitivity. A hydrogen lamp was used as the light source.

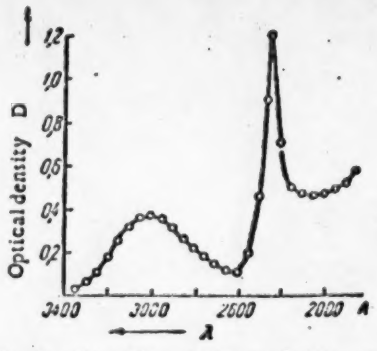

Fig. 2. Absorption spectrum of an aqueous solution of pertechnate.

An aqueous solution of ammonium pertechnate was examined. The technetium concentration in the sample was determined radiometrically and equalled $2.9 \cdot 10^{-4}$ M (approximately 400 counts/min).

The absorption curve, illustrated in Fig. 2, is similar to the curve obtained by the other investigators [3, 4]. However, the maximum at 2450 A, which we found, is approximately 20 A closer to the short wave region. In our case, the value of the molar extinction coefficient $E = D/C = 1.276/0.00029 = 4407$. A molar extinction coefficient of 4000 at an absorption maximum of 2470 A is reported in the literature. The slight deviation from literature data observed, may be explained by the fact that the measurements were performed on different spectrophotometer models with different resolving capacities.

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THE CONNECTION BETWEEN THE ACID NATURE OF TRICALCIUM PHOSPHATE AND ITS CATALYTIC ACTIVITY IN HYDROLYSIS REACTIONS

L. Kh. Freidlin and V. Z. Sharf

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

(Presented by Academician A. A. Balandin, September 2, 1958)

In a series of previous works it was established that tricalcium phosphate has a high activity in dehydration [1], hydration [2] and vapor-phase hydrolysis of halobenzenes [3]. It was proposed that the activity of the phosphate in these reactions was caused by its acid nature. If this is correct, then the catalytic activity of the phosphate should be reduced in the presence of bases. In order to test this proposition, in the present work, a study was made of the hydrolysis of vinyl ethers on tricalcium phosphate and its deactivation by bases – amines and alkali hydroxides. This reaction was chosen as the hydrolysis of vinyl ethers (in the liquid phase) is strongly catalyzed by acids, but is not accelerated by bases. The hydrolysis of alkyl vinyl ethers in the vapor phase is accelerated by aluminosilicate, silver oxide [4] and tungsten dioxide on aluminum oxide [5].

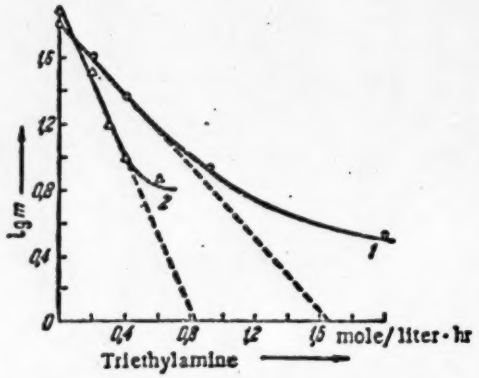

Fig. 1. Deactivation of a phosphate catalyst by triethylamine in the hydrolysis of vinyl phenyl (1) and vinyl 2,4-dichlorophenyl (2) ethers.

The experiments were carried out in a circulating apparatus [2]. The catalyst was prepared from calcium chloride and diammonium phosphate. The reaction tube was Pyrex, the volume of catalyst 5 ml and the grain size 2 x 3 mm. All the experiments were performed with one and the same portion of catalyst. After each experiment, lasting about 1 hour, the catalyst was regenerated by treatment with air at 400° for 2 hours. With the aid of two automatic dosers, the ether and water were introduced equally through an evaporator onto the catalyst and the amine was mixed with either the ether or the water. The rates of introduction of the amines, ethers and water were calculated in moles per liter of catalyst per hour. In experiments with vinyl phenyl and vinyl 2,4-dichlorophenyl ethers, the catalyzate was placed in a flask connected to a reflux condenser and the acetaldehyde distilled off in a stream of nitrogen by boiling and absorbed in water. Then to the catalyzate was added an aqueous solution of sodium hydroxide and the mixture treated three times with n-heptane to extract the unreacted ether.

The acetaldehyde (acetone) content of the reaction products was determined by the oxime method, the phenol, bromometrically and the unreacted ether by the consumption of hydrogen during its hydrogenation over Raney nickel at 20°. In experiments with α-methylvinyl aryl ethers, a correction was introduced in the determination of acetone to allow for its incomplete oximination [6]. In experiments with vinyl n-butyl ether and with 4,5-dihydrosylvan the acetaldehyde and acetopropyl alcohol in the catalyzate were determined by oximination in an alkaline medium [7].

The constants of the compounds hydrolyzed and the conditions and results of the experiments are given in the Table, showing that the hydrolysis proceeds at a relatively rapid rate at comparatively low temperatures on the phosphate catalyst. Vinyl n-butyl, α-methylvinyl phenyl and α-methylvinyl m-cresyl ethers and 4,5-dihydrosylvan are hydrolyzed almost quantitatively at 160° and vinyl phenyl and vinyl 2,4-dichlorophenyl ethers are 65 and 77% hydrolyzed, respectively. In the absence of catalyst, vinyl n-butyl ether, for example, is only 3% hydrolyzed (Exp. No. 21) at a higher temperature (220°). In experiments with vinyl phenyl and vinyl 2,4-dichlorophenyl ethers, the yield of phenol is usually higher than the yield of acetaldehyde. The latter probably

TABLE

Expt. no.	Hydrolyzed ether (b.p.; n_D^{20}; d_4^{20})	Experimental conditions: temp., °C	molar ratio, water : ether	introd. rates water – ether mixture, M/liter	introd. rates triethylamine, M/liter	Yield, %: phenols	acetaldehyde
1	Vinyl phenyl (154–155°; 1,5226; 0,9772)	160	12 : 1	68	0	65,0	59
2		160	12 : 1	68	0,205	40,5	18
3		160	12 : 1	68	0,411	23,4	9
4		160	12 : 1	68	0,904	8,8	4
5		160	12 : 1	68	1,979	3,5	1
6		160	12 : 1	68	2,400[1]	36,4	23
7	Vinyl 2,4-dichlorophenyl (85–87°/7 mm 1,5568; 1,2828)	160	14,5 : 1	68	0	77,0	62
8		160	14,5 : 1	68	0,205	34,0	16
9		160	14,5 : 1	68	0,307	16,1	9
10		160	14,5 : 1	68	0,411	11,0	5
11		160	14,5 : 1	68	0,614	7,6	3
12		160	14,5 : 1	68	2,400[1]	41,0	29
12a		160	14,5 : 1	68	0	3,3	1
12b		160	14,5 : 1	68	0	82,5	71
13	α-Methylvinyl phenyl (61°/18 mm 1,5050; 0,9551)	160	14 : 1	68		96,0	98[3]
14	α-Methylvinyl m-cresyl (79°/10 mm 1,5051; 0,9444)	160	15 : 1	67			97[3]
15	Vinyl n-butyl (93–94°; 1,4038; 0,7790)	94	6,8 : 1	115			10
16		140	6,8 : 1	115			95
17		160	1 : 1	115			38
18		160	2 : 1	115			62
19		160	6,8 : 1	115			97
20		200	6,8 : 1	115			91
21[4]		220	6,8 : 1	115			3
22		300	6,8 : 1	115			84
23	4,5-Dihydrosylvan (79–80°; 1,4297; 0,9039)	160	9,2 : 1	66			98[2]

Note: [1] Pyridine. [2] Acetopropyl alcohol. [3] Acetone. [4] Experiment in the absence of catalyst.

undergoes partial condensation under the conditions of the process. The same may explain the fall in acetaldehyde yield from vinyl n-butyl ether at temperatures above 160°. In Experiments Nos. 1-5, the amount of unreacted ether in the catalyzate was determined besides the phenol and the acetaldehyde. The presence of triethylamine did not interfere with the determination of the ether, but pyridine completely deactivated the nickel hydrogenation catalyst. The amounts of ether in these experiments were respectively 29.0, 65.7, 75.1, 89.3 and 93.4%. Thus, the total of phenol and unreacted ether reached 94.0-98.3%.

Experiments Nos. 1-12, in which the effect of bases on the catalyst activity was studied, were of the greatest interest. In the presence of triethylamine, the degree of hydrolysis of vinyl aryl ethers fell sharply. In the presence of large amounts of triethylamine, the hydrolysis of ethers stopped almost completely. Apparently, triethylamine adsorbed on the catalyst is continuously desorbed and carried by the stream of water vapor. This is confirmed by the fact that when a catalyst that had been strongly deactivated with triethylamine (after Experiment No. 5) was treated with water vapor (5.7 ml of water per hour at 160° for 2 hours), its activity was completely restored, indicating complete desorption of the amine. Consequently, only part of the amine is held on the catalyst and the greater this is, the higher its concentration in the reaction sphere.

Figure 1 shows the dependence of the logarithm of the degree of hydrolysis (lg m) of vinyl aryl ethers (calculated on the phenol yield) on the amount of triethylamine passed through. The curves indicate that there is an exponential relation between the activity of the catalyst and the amount of triethylamine introduced into the sphere of the reaction. A similar dependence was observed in paper [8], in which a study was made of the poisoning of an aluminosilicate catalyst by organic bases in the cracking of hydrocarbons. However, as Fig. 1 shows, a further increase in the amount of triethylamine passed over the catalyst (> 0.4 mole/liter·hour in the reaction with vinyl 2,4-dichlorophenyl ether and 0.6 mole/liter·hour in experiments with vinyl phenyl ether) had a considerably lower deactivating effect. Probably, considerable saturation of the catalyst surface with triethylamine had already been reached at these concentrations. It is interesting that the deactivating effect of a considerably weaker base, pyridine, is extremely weak in comparison with triethylamine (Experiments Nos. 6 and 12). This indicates that the poisoning effect of triethylamine is connected with its basic properties.

It was natural to expect that the catalyst could also be deactivated by mineral bases. Actually, after the catalyst (3.15 g) had been treated with potassium hydroxide (0.0581 g), it was almost completely deactivated (Experiment No. 12a). For restoring its activity, the catalyst was treated with a 50% aqueous solution of acetic acid, washed with water and then regenerated to remove the excess acetic acid. Experiment No. 12b shows that the activity of the catalyst was almost completely restored.

Thus, the result of our work shows that tricalcium phosphate has a high catalytic activity in the hydrolysis of vinyl ethers.

In the presence of bases, the activity of the catalyst falls sharply and hydrolysis of the ether may be stopped almost completely. These facts confirm the propositions on the acid nature of a phosphate catalyst.

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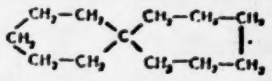
SYNTHESIS OF SPIRO-(5,6)-DODECANE

N. V. Elagina and Academician B. A. Kazanskii

M. V. Lomonosov Moscow State University

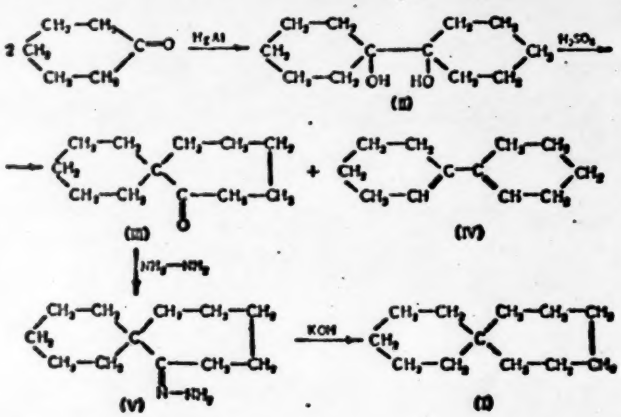
In previous communications, syntheses were described for some cyclic hydrocarbons containing a quaternary carbon atom in the ring, namely, spiro-(4,4)-nonane [1], spiro-(4,5)-decane [2] and 1,1-dimethylcyclohexane [3,4], involving the use of the pinacolin rearrangement of ditertiary α-glycols. The ketones obtained in this way were converted into hydrazones and the latter were decomposed catalytically by the method of N. M. Kizhner.

In the present work this reaction was used for the synthesis of yet another bicyclic hydrocarbon with a spirane structure – spiro-(5,6)-dodecane (I).



(I)

First, cyclohexanone was reduced with amalgamated aluminum in dry benzene to give 1,1'-dihydroxydicyclohexyl (II). The pinacone (II) was treated with 63% sulfuric acid to give a mixture containing 30% of spiro-(5,6)-dodecanone-7 (III) and 70% 1,1'-dicyclohexenyl (IV). As our experiments showed, the use of higher sulfuric acid concentrations led to tar formation and more dilute sulfuric acid acted mainly as a dehydrating agent so that the main reaction product was 1,1'-dicyclohexenyl (IV).



The mixture of ketone (III) and diene (IV) was distilled in vacuum on a fractionating column and the fractions enriched in spiroketone were treated with semicarbazide hydrochloride. The semicarbazone of spiro-(5,6)-dodecanone-7 was decomposed with hydrochloric acid and the ketone distilled off in steam. Treatment of spiro-(5,6)-dodecanone-7 (III) with hydrazine hydrate gave the hydrazone (V), which was decomposed in the presence of potassium hydroxide and platinized charcoal.

The spiro-(5,6)-dodecane obtained was a quite thick, colorless liquid with a pleasant camphor-like smell.

The constants of spiro-(5,6)-dodecane are as follows: b.p. 100-101°/9 mm; $n^{20}D$ 1.4874; d^{20}_4 0.9021; MR_D found 53.06, calculated for $C_{12}H_{22}$ 53.21.

EXPERIMENTAL

1,1'-Dihydroxy-1,1'-dicyclohexyl. Into a 2 liter round-bottomed flask, connected to a reflux condenser and a dropping funnel through an adaptor, was placed 50 g (1.9 g-at) of fine aluminum turnings and 400 ml of dry benzene. The benzene was heated to boiling and then a solution of 24 g of mercuric chloride in 200 g (2.04 mole) of freshly distilled cyclohexanone was added. A vigorous reaction began immediately and was accompanied by energetic boiling of the reaction mixture, which continued for 15 minutes. The mixture was then boiled on a water bath with frequent shaking for 1 hour. 160 ml of water and 200 ml of benzene were added to the cooled reaction mixture. The reaction mixture was heated on a boiling water bath for 1 hour and filtered in the hot state through a Buchner funnel. The residue was extracted with 250 ml of boiling benzene and the benzene solution separated from the residue on a Buchner funnel. This operation was carried out two more times. The benzene solutions were combined and benzene distilled off until temperature of the emergent vapors reached 120°.

The residue in the flask, a thick yellow oil, was cooled with ice. When petroleum ether was added, a white crystalline precipitate of the pinacone formed and this was sucked off, washed with petroleum ether and dried in air. We obtained 91.7 g of 1,1'-dihydroxy-1,1'-dicyclohexyl (yield 45.4% of theoretical) with m.p. 129-130°.

Literature data: m.p. 128.5-129.5 [5]; 130° [6-8]; 128° [9].

Spiro-(5,6)-dodecanone-7 and 1,1'-dicyclohexenyl. Into a 500 ml round-bottomed flask, connected to a reflux condenser through an adaptor, was placed 100 ml of water and 100 ml of concentrated sulfuric acid (d 1.84). 69 g (0.3 mole) of finely ground 1,1'-dihydroxy-1,1'-dicyclohexyl was gradually added with shaking to the still warm mixture. Turbidity of the solution was observed and an oily layer formed on the surface. The flask was heated for 2 hours on a boiling water bath with frequent shaking. After the heating, the reaction mixture consisted of two layers, an upper, yellow oily layer, containing the spiroketone and the diene hydrocarbon and a lower, aqueous layer. The oil was steam distilled and the distillate extracted with ether.

The ether solution was washed with 3% sodium hydroxide solution and then with water and dried over fused potassium carbonate. The ether was removed and the residue fractionated in vacuum. We obtained 27.5 g of a mixture of spiro-(5,6)-dodecanone-7 and 1,1'-dicyclohexenyl, which had b.p. 103-103.5°/2 mm and n 1.5258.

The semicarbazone of spiro-(5,6)-dodecanone-7. A mixture of spiro-(5,6)-dodecanone-7 and 1,1'-dicyclohexenyl (286 g) was fractionally distilled in vacuum on a fractionating column with glass packing with an efficiency of 40 theoretical plates. Fractions enriched in spiroketone (b.p. 125°/9 mm, $n^{20}D$ 1.4973 and b.p. 126.8-127°/10 mm; $n^{20}D$ 1.4988) were treated with semicarbazide hydrochloride. The semicarbazone was sucked off, washed on the filter with alcohol, water, again with alcohol and with petroleum ether and recrystallized twice from a 15-fold amount of ethyl alcohol. We obtained 128 g of the semicarbazone of spiro-(5,6)-dodecanone-7 with m.p. 206-207°.

Literature data: m.p. 208.5-209.5° [10]; 209.5-210.5° [11].

Spiro-(5,6)-dodecanone-7. Into a round-bottomed flask of 500 ml capacity was placed 20 g (0.084 mole) of the semicarbazone of spiro-(5,6)-dodecanone-7 and 200 ml of 10% hydrochloric acid. The flask was fitted with a reflux condenser and heated on a boiling water bath for 2 hours with shaking. The ketone liberated was steam distilled. The distillate was extracted with ether.

The ether solution was washed with 3% soda solution and then with water and dried over anhydrous magnesium sulfate. The ether was distilled off and the residue vacuum distilled.

128 g of the semicarbazone of spiro-(5,6)-dodecanone-7 yielded 88 g of spiro-(5,6)-dodecanone-7. The yield, calculated on 1,1'-dihydroxy-1,1'-dicyclohexyl, was 15.5% of the theoretical.

The constants of spiro-(5,6)-dodecanone-7 were as follows: b.p. 110°/4 mm; 119-120°/7 mm; $n^{20}D$ 1.4942; d^{20}_4 0.9906; MR_D found 53.00, calculated for $C_{12}H_{22}O$ 53.22.

Literature data: b.p. 120°/8 mm, $n^{24}D$ 1.4830, d^{24}_4 0.9795 [8]; b.p. 101-103°/2 mm [10]; b.p. 129-131°/12 mm [11].

Spiro-(5,6)-dodecane. Into a 150 ml round-bottomed flask, fitted with a reflux condenser, was placed 34.6 g (0.19 mole) of spiro-(5,6)-dodecanone-7, 31.7 g (.57 mole) of 90% hydrazine hydrate and 50 ml of ethyl alcohol. The flask was heated for 7 hours on an oil bath; the temperature was kept at 120°. Then the alcohol and the unreacted hydrazine hydrate were distilled from the reaction mixture. At the end of the distillation, the temperature of the bath was raised to 140°.

The residue in the reaction flask was saturated with solid potassium hydroxide and the floating hydrazone was separated from the aqueous layer in a separating funnel. The hydrazone was dried with freshly fused potassium hydroxide, first in the cold and then with heating on an oil bath at 100°. We obtained 36.3 g of the hydrazone of spiro-(5,6)-dodecanone-7 in the form of a thick, light yellow oil.

The hydrazone of spiro-(5,6)-dodecanone-7 was decomposed catalytically without preliminary distillation.

Into a 100 ml Wurtz flask, fitted with a thermometer and connected to a distillation condenser, was placed the hydrazone of spiro-(5,6)-dodecanone-7 and 2 g of freshly fused potassium hydroxide, ground to a fine powder, with 0.1 g of platinized charcoal. The mixture was heated on a metal bath, whose temperature was slowly raised. The hydracarbon distilled off at a bath temperature of 240-250°. The temperature of the emergent vapor was 210-215°. The distillate was dried with fused potassium hydroxide and distilled over fresh catalyst. The hydrocarbon obtained was washed three times with 50% acetic acid, then with water, with 3% potassium hydroxide solution and again with water and dried with fused potash. Fractionation over metallic sodium yielded 18.3 g of spiro-(5,6)-dodecane. The yield was 57.3% of theoretical.

The constants of spiro-(5,6)-dodecane were as follows: b.p. 100-101°/9 mm; $n^{20}D$ 1.4874; d^{20}_4 0.9021; MP_D found 53.06, calculated for $C_{12}H_{22}$ 53.21.

Found %: C 86.64; 86.64; H 13.25; 13.46 $C_{12}H_{22}$. Calculated %: C 86.66; H 13.34

Spiro-(5,6)-dodecane was a quite thick, colorless liquid with a camphor-like smell.*

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* On reducing 15 g of spiro-(5,6)-dodecanone-7 by the Clemmensen method, Laber [12] obtained a tarry product, from which he was able to isolate a very small amount of a fraction with b.p. 103-106°/9 mm and $n^{20}D$ 1.4890.

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INVESTIGATION OF THE COMPOSITION OF URANATES OF ALKALI ELEMENTS PREPARED BY A DRY METHOD

K. M. Efremova, E. A. Ippolitova, Yu. P. Simanov and Academician V. I. Spitsyn

M. V. Lomonosov Moscow State University

In the literature there are reports [1-3] on the preparation of monouranates of all the alkali metals and the diuranates of lithium, sodium and potassium by the high temperature reaction of uranium oxides or salts with the oxides or salts of alkali elements. Fusion of uranyl sulfate with sodium or potassium chloride followed by boiling the reaction product with water gave sodium triuranate, $Na_2U_3O_{10}$, and the hexahydrate of potassium hexauranate, $K_2U_6O_{19} \cdot 6H_2O$, respectively. It is reported [4] that on reacting UO_3 with molten sodium hydroxide first a uranate with the composition Na_4UO_5 is formed and then (above 400°) this is converted into a more stable compound in which the ratio of Na:U varies from 0.5:1 to 1:1. Thus, there are no exhaustive data on the nature of the uranates formed by each alkali element at high temperatures.

TABLE 1

Firing of Normal Uranates of Alkali Elements. The Duration of Firing at Each Temperature was 6 Hours

Temp. °C	The ratio of $Me_2O:UO_3$ in the firing products				
	Li_2UO_4	Na_2UO_4	K_2UO_4	Rb_2UO_4	Cs_2UO_4
700	1:1	1:1	1:1,005	1:1,005	1:1,013
800	1:1	1:1,01	1:1,018	1:1,022	1:1,12
900	1:1	1:1,015	1:1,023	1:1,06	1:1,62
1000	1:1	1:1,02	1:1,036	1:1,28	1:2,47
1100	1:1	1:1,05	1:1,07	1:1,97	1:3,12

Zachariasen [5] reports that the structures of lithium, sodium and potassium monouranates contain hexagonal or pseudohexagonal layers, similar to those in calcium monouranate [6]. However, the results obtained by other authors [7] do not agree with the data given by Zachariasen. They found that the structures of α-Li_2UO_4, β-Na_2UO_4, K_2UO_4, Rb_2UO_4 and Cs_2UO_4 contained tetragonal or pseudotetragonal layers of $(UO_2)O_2$, similar to those reported for the structures of $BaUO_4$ [8] and β-$UO_2(OH)_2$ [9]. It is possible that this difference is due to the existence of polymorphous modifications. Hexagonal layers of the composition $UO_{3.5}$ were found in the structures of sodium, potassium and rubidium diuranates [7].

Using thermal and x-ray phase analysis, we investigated the preparation conditions and the composition of uranates of alkali elements formed by heating uranium oxides (UO_3 or U_3O_8) in air with the carbonates of the appropriate elements. The thermal analysis was carried out with a PK-52 pyrometer using compressed tablets.

In investigating the reaction of uranium oxides with the carbonates of alkali elements, the reagents were taken in amounts calculated to give uranates with different ratios of Me_2^IO and UO_3 (3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6).

Lithium uranates. The existence of Li_4UO_5, α-Li_2UO_4, β-Li_2UO_4, $Li_2U_2O_7$ and $Li_2U_3O_{10}$ was established. α-Li_2UO_4 was converted to β-Li_2UO_4 as a result of prolonged firing (60 hours) at 1300°. No lithium diuranate formed when Li_2UO_4 was heated in a current of CO_2. β-Li_2UO_4 crystallized in hexagonal syngony, as Zachariasen had supposed [5]. The axis parameters are a = 3.96 kX, z = 2. Li_4UO_5 crystallized in rhombic syngony with axis parameters of a = 10.97 ± 0.01 kX, b = 7.95 kX, c = 4.98 ± 0.01 kX, $\rho_{x\text{-ray}} = 5.12$, $\rho_{pyk} = 4.81$ and z = 4. The crystals of lithium triuranate are of tetragonal syngony with axis parameters of a = 5.62 ± 0.01 kX, c = 12.28 ± 0.02 kX, $\rho_{x\text{-ray}} = 7.62$, $\rho_{pyk} = 7.23$ and z = 2.

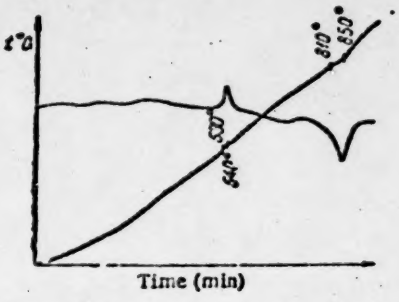

Fig. 1. The heating curve of the mixture Na_2CO_3 and UO_3 (1:1).

Sodium uranates. The investigations established the formation of Na_4UO_5, α- and β-modifications of Na_2UO_4 and $Na_2U_2O_7$. Regardless of the ratio of the reagents, the reaction of uranium oxides with sodium carbonate started at about 500°. In all cases the exothermic effect on the thermograms corresponded to the formation of sodium diuranate. For example, the heating curve of a mixture with the ratio of Na_2CO_3: UO_3 = 1:1 (Fig. 1) had two effects: exothermic (530-540°), the effect of the components reacting, and endothermic (825-850°), corresponding to the melting of the sodium carbonate that had not reacted.

To investigate the further course of this reaction, separate portions of this mixture were fired to constant weight at 600-650° and at higher temperatures. The x-rays of the fired products indicated that at temperature of 600° the diuranate, reacting with excess sodium carbonate, was converted to sodium α-monouranate. This reaction proceeded slowly and therefore no effect corresponding to it was observed on the thermogram.

The heating curve of sodium α-monouranate (Fig. 2) showed that at a temperature of 900-925° (endothermic effect) it was converted to the β-modification of sodium monouranate. Heating Na_2UO_4 in a current of CO_2 (4 hours and 1000°) gave sodium diuranate.

Firing a mixture of Na_2CO_3 and UO_3 in a ratio of Na_2O: UO_3 = 2:1 and 3:1 at 1000° gave a uranate of the composition Na_4UO_5. Its formation proceeded through the stages of di- and monouranates. Na_4UO_5 crystallized in rhombic syngony with axis parameters of a = 10.91 ± 0.02 kX, b = 5.71 kX, c = 5.02 ± 0.01 kX, $\rho_{x\text{-ray}} = 5.07$, $\rho_{pyk} = 4.71$ and z = 2. On investigating the firing products of the other mixtures (1:2; 1:3 etc.) we noted only the formation of sodium diuranate.

Potassium uranates. On investigating the reaction of uranium oxides with potassium carbonate it was found that as reported above, at first, regardless of the ratio of the starting reagents, potassium diuranate was formed and, depending on whether there was an excess of potassium carbonate or uranium oxide, this was converted to potassium ortho-, mono- or triuranate. Suitable ratios of $K_2U_2O_{10}$ and U_3O_8 reacted to give tetra- and hexauranates.

Thus, the reactions in the solid phase gave K_4UO_5, K_2UO_4, $K_2U_2O_7$, $K_2U_3O_{10}$, $K_2U_4O_{13}$ and $K_2U_6O_{19}$. K_4UO_5 crystallized in rhombic syngony with axis parameters of a = 12.92 kX, b = 3.49 kX, c = 8.57 kX, $\rho_{x\text{-ray}} = 4.19$, $\rho_{pyk} = 4.10$ and z = 2.

Rubidium uranates. The formation of Rb_4UO_5, Rb_2UO_4, $Rb_2U_2O_7$, $Rb_2U_4O_{13}$, and $Rb_2U_6O_{19}$ was established. As in the previous cases, the monouranate and salts with the composition Rb_4UO_5 formed through the stage of diuranate. Rb_4UO_5 crystallized in tetragonal syngony with axis parameters of a = 8.16 kX, c = 13.7 kX, $\rho_{x\text{-ray}} = 6.00$, $\rho_{pyk} = 5.51$ and z = 4.

Cesium uranates. Cs_2CO_3 reacted with uranium oxides to give uranates with the following composition: Cs_2UO_4, $Cs_2U_2O_7$, $Cs_2U_3O_{10}$, $Cs_2U_4O_{13}$, $Cs_2U_6O_{19}$ and Cs_2UO_4 was also formed through the stage of diuranate. A comparison of the data on the composition of the uranates of various alkali elements showed that the most complex polyuranates (tetra- and hexauranates) formed only with alkali metals which have the greatest radii (K, Rb and Cs). In this case these large anions are stable, due to the low polarizing effect of the cations.

The data available in the literature [1] on the behavior of uranates under high temperature conditions do not give a complete picture of the thermal stability of these salts.

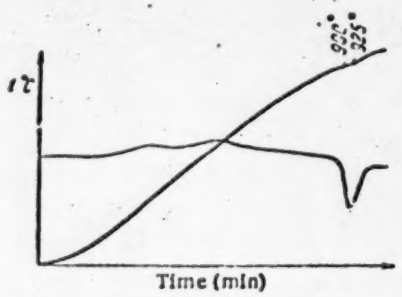

Fig. 2. The heating curve of sodium monouranate.

We investigated the thermal stability of the uranates obtained. Samples of monouranates, reduced to constant weight at 600°, were heated in a platinum boat in a current of air for 6 hour periods at temperatures of 700-1100° at 100° intervals. The data obtained are given in the Table. The firing products were investigated by x-ray phase analysis.

Lithium monouranate is heat stable as it does not decompose when heated for 60 hours at 1300°. In contrast to Li_2UO_4, sodium, potassium and rubidium uranates decompose at temperatures of 1200-1300° to give diuranates. Na_2UO_4 was completely converted to $Na_2U_2O_7$ when fired at 1300° for 74 hours. K_2UO_4 at 1200° for 60 hours and Rb_2UO_4 at 1200° for 12 hours. Cs_2UO_4 decomposed when fired at 1200° for 6 hours.

Thus, in going from Li_2UO_4 to Cs_2UOR_4 the stability of the monouranates decreases and this corresponds to the increase in the deformability of the cations in this order and in the volatility of the oxides [10].

Sodium and potassium diuranates were completely stable at 1300°; rubidium diuranate, fired at 1200° for 30 hours, changed its structure which indicates either the appearance of a new modification or partial decomposition (the color of the uranate remained orange). Cesium diuranate decomposed at 1200°.

The thermal decomposition of potassium triuranate occurred at 1100-1200° and was accompanied by a change in color from orange to black. This gave $K_2U_2O_7$ and U_3O_8 by the reaction:

$$3K_2U_3O_{10} \rightleftarrows 3K_2U_2O_7 + U_3O_8 + 0{,}5O_2$$

Slow cooling of the firing products as well as heating them in air at a temperature of 800-900° produced the reverse reaction and orange red potassium triuranate was reformed.

Of the polyuranates we prepared, rubidium tetrauranate was the most stable compound – it did not decompose when heated at 1200° for 30 hours. Rubidium hexauranate decomposed at 900° to form mixed oxides of uranium.

When cesium mono-, di-, tri- and tetrauranates were heated at 1200° for 6 hours and cesium hexauranate at 1000° (6 hours), the color changed from orange to black. An x-ray phase analysis of the firing products showed that they contained the same phase with a uranium content of 68.7%. Besides this phase, the firing product of cesium hexauranate also contained mixed oxides of uranium.

Thus, the hexauranates of alkali elements are less stable than the other polyuranates.

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APPLICATION OF HAMMETT'S EQUATION IN THE THEORY OF TAUTOMERIC EQUILIBRIUM

THE THIONE-THIOL TAUTOMERISM OF THIOPHOSPHORUS COMPOUNDS

Academician M. I. Kabachnik, T. A. Mastryukova, A. E. Shipov and T. A. Melent'eva

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

As was shown previously [1], the relation of the equilibrium constant to the ionization constant of the form, $K_{1S} = K_{1S}/K_{2S}$, or on introducing the activity coefficients referred to a single standard medium, $K_{TS} = (K_1/K_2)(f_{1S}/f_{2S})$ is of fundamental importance in the theory of tautomeric equilibrium. On this basis the Bronsted-Izmailov theory [2] of acid-base protolytic equilibrium in solution was applied to tautomeric equilibrium and, thus, a quantitative interpretation of the ionic theory tautomerism was proposed. Two of us and S. T. Ioffe showed that the Bronsted equation is applicable to thiophosphoroorganic acids. This made it possible to determine the position of tautomeric equilibrium in dialkyl dithiophosphoric acids [3] and (with N. I. Kurochkin, E. M. Popov and N. P. Rodionova) in alkyl thioalkylphosphinic acids [4].

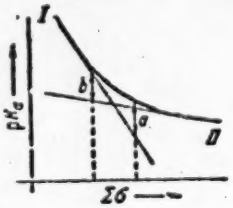
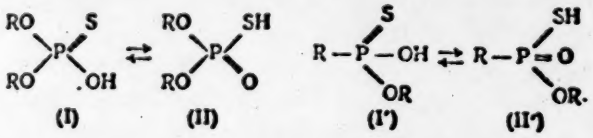


Fig. 1



In this work attention was mainly paid to the effect of the medium on the position of the equilibrium. The effect of the structure of the tautomeric forms was considered only qualitatively on the basis of the qualitative rules of organic chemistry.

It was important to proceed further and establish the principles of the quantitative relation of the structure of tautomeric acids to the position of the equilibrium. As the tautomeric equilibrium constant is a function of the acid properties of the forms participating in the equilibrium, it is possible to use the known quantitative rules which relate the structure of organic acids to their ionization constants. This type of rule is described by Hammett's law [5] $\log (K/K^0) = \rho\sigma$. Hammett's equation is applicable to various aromatic compounds. One of us showed recently that it is also applicable (in the form $pK = pK^0 - \rho\Sigma\sigma$) to organophosphorus acids of the type RR'P(O)OH or RR'P(S)OH (R and R' are hydrogen, hydroxyl, alkoxyl, aroxyl or different aliphatic or aromatic radicals) [6]. In this case, the conducting system (instead of an aromatic ring) is a phosphoryl or a thiophosphoryl group.

It was thus reasonable to use Hammett's equation in studying the tautomerism of thiophosphorus compounds. One could assume that the methods of investigation developed and the rules established on the example of thiophosphorus compounds would be general and, consequently, could be further used for studying other forms of tautomerism.

In applying Hammett's rule to the ionization constants of two tautomeric forms, it is necessary to write two linear equations:

$$pK_1 = pK_1^0 - \rho_1\Sigma\sigma, \quad (a) \qquad pK_2 = pK_2^0 - \rho_2\Sigma\sigma \quad (b), \tag{1}$$

which differ only in the values of the parameters pK^0 and ρ (ρ_1 for form (I) and ρ_2 for form (II)). In the general case, they are expressed graphically in the coordinates pK and $\Sigma\sigma$ by two intersecting lines (Fig. 1). Since $pK_T = pK_1 - pK_2$, then the constant of the tautomeric equilibrium in this graph is characterized for each substance (each value of $\Sigma\sigma$) by the segment of ordinate b, included between the two lines. The point of intersection of the lines (b = 0) corresponds to $K_T = 1$. The region to the left of this point corresponds to the displacement of the tautomeric equilibrium toward form (I) and that to the right toward form (II).

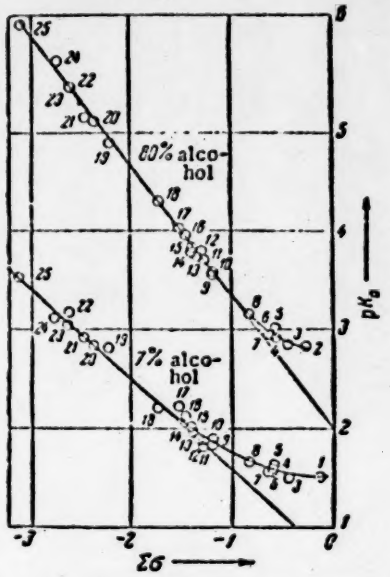


Fig. 2

Experimentally, however, it is not the ionization constants of separate forms which are measured but certain effective constants K_a, related to the ionization constants of the forms by the equation [7]

$$K_a = K_1K_2/(K_1 + K_2). \tag{2}$$

Thus, if $K_1 \gg K_2$, then $K_a = K_2$ and, on the contrary, if $K_1 \ll K_2$, then $K_a = K_1$. If K_1 and K_2, taken from formulas (1a) and (1b), are substituted in equation (2), then the relation of K_a to the parameters of Hammett's equation may be readily derived:

$$K_a = \frac{K_1^0 K_2^0 \cdot 10^{(\rho_1+\rho_2)\Sigma\sigma}}{K_1^0 \cdot 10^{\rho_1\Sigma\sigma} + K_2^0 \cdot 10^{\rho_2\Sigma\sigma}}. \tag{3}$$

This relation is expressed graphically in the coordinates pK and $\Sigma\sigma$ by the curve $pK_a = \varphi(\Sigma\sigma)$, which approaches asymptotically the two upper legs of lines I and II (Fig. 1). This curve passes above the point of intersection of the two lines at a distance (along the ordinate) of log 2.*

If we take logarithms of equation (2) we obtain $pK_a = pK_1 - \log K_2/(K_1+K_2)$, and hence $pK_a - pK_1 = \log(K_T + 1) = a$; finally

$$K_T = 10^a - 1, \tag{4}$$

where a is the deviation (along the ordinate) of the experimental curve from its asymptote, which coincides with the line $pK_1 = pK_1^0 - \rho_1\Sigma\sigma$. The experimental method of solving the problem quantitatively is based on this.

The effective ionization constants of tautomeric mixtures of a series of similar substances, which differ in the nature of the substituents (in the case of thiophosphoroorganic acids—R or R'), are measured by some method. The graph $pK = \varphi(\Sigma\sigma)$ is plotted from the data obtained. If a linear relation is thus obtained, then one may conclude that the tautomeric equilibrium of all the substances investigated is displaced practically completely toward one form. If, however, the experimental data result in a curve, of which only one branch corresponds to a linear relation while the other deviates from it, then one may conclude that the equilibrium is displaced toward one of the forms of the substances which corresponds to the linear section of the curve and that a second form appears in the equilibrium in the region of the deviation. The ordinate segments a, included between the experimental curve and the line, obtained by extrapolating the linear section, characterize the value of the tautomeric equilibrium constant according to formula (4). We give the experimental data obtained for thiophosphoroorganic compounds.

* Recently Jaffé and Gardner [8] derived a similar equation for a particular case when $K_1^0 = K_2^0$, namely, for the tautomerism of salts of substituted azobenzenes: $K_a = K^0(10^{\rho_1\sigma} \cdot 10^{\rho_2\sigma})/(10^{\rho_1\sigma} + 10^{\rho_2\sigma})$; however, they did not give the solution of the problem.

Table 1 gives the effective ionization constants (pK_a) for a series of tautomeric acids RR'P(S)OH ⇌ RR'P(O)SH, which differ in the groups R and R' and, consequently, in the values of $\Sigma\sigma$, calculated according to [6 and 9]. The determinations were carried out by potentiometric measurement of the pH of partially neutralized solutions in 7 and 80% alcohol (LP-5 pH-meter, adjusted with a biphthalate buffer with pH 4.00; concentration $5 \cdot 10^{-3}$ mole/liter; temperature 20° and determination error ± 0.05 pK). As Fig. 2 shows, a good linear relation of the points with $\Sigma\sigma$ from −3 to −1 was observed in 80% alcohol. In 7% alcohol deviation from a linear relation began at lower values of $\Sigma\sigma$ so that it was preferable to use only the points with $\Sigma\sigma$ from −3 to −2 to obtain a reliable linear extrapolation. The parameters of the lines $pK_1 = pK_1^0 - \rho_1\Sigma\sigma$, characterizing the ionization constants of thione forms in 7 and 80% alcohol were found from the data obtained (by the method of least squares [10]). The following results were obtained: in 7% alcohol $pK_1 = 0.69 - 0.924\,\Sigma\sigma$ with a correlation coefficient of $r = 0.962$; and in 80% alcohol $pK_1 = 2.00 - 1.329\,\Sigma\sigma$ with $r = 0.998$. From this we calculated the values of the deviation a from a linear relation for points lying on the curved sections, and the values of K_T corresponding to them (equal to $10^a - 1$), given in Table 1.

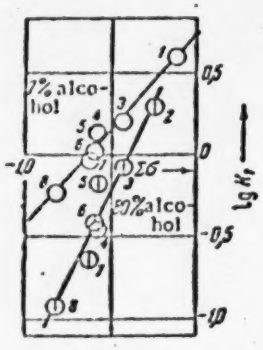


Fig. 3

The values of the tautomeric equilibrium constants must, in their turn, satisfy Hammett's equation:

$$\log K_T = \log K_T^0 + \rho_T \Sigma\sigma. \qquad (5)$$

Fig. 3 shows the graph of the relation of log K_T to $\Sigma\sigma$, plotted from the data in Table 1. As can be seen, the linear relation of Hammett is fulfilled here quite well. Further elaboration (by the method of least squares) gave

TABLE 1

Expt. no.	R	R'	B.p., °C	P, mm	n_D^{20}	d_4^{20}	$\Sigma\sigma$	pK_a alcohol 7%	pK_a alcohol 80%	a alcohol 7%	a alcohol 80%	K_T alcohol 7%	K_T alcohol 80%	% thiol form 7% alcohol present work	% thiol form 7% alcohol [3 and 4]	% thiol form 80% alcohol present work	% thiol form 80% alcohol [3 and 4]
1	C_6H_5O	C_6H_5O [1]	m.p. 86—87				−0.122	1.50	—[2]	0.70	—	4.01	—	80		79	
2	CH_3O	CH_3O [1]	m.p. 156 with decomp.				−0.268	—[3]	2.60	—	0.47	—	1.99	74	72	68	72
3	C_6H_5O	C_6H_5O	106—107	2.5	1.4719	1.1800	−0.428	1.49	2.84	0.41	0.27	1.57	0.86	64	70	46	71
4	iso-C_3H_7O	iso-C_3H_7O	89—90	1.5	1.4592	1.0200	−0.582	1.59	2.80	0.37	0.13	1.34	0.35	54	74	29	73
5	p-ClC_6H_4	p-ClC_6H_4	m.p. 103—104				−0.594	1.00	3.00	0.32	0.22	1.34	0.66	54		28	
6	iso-C_3H_7O	iso-C_3H_7O	82,5—84	0.05	1.4570	1.0356	−0.600	1.55	2.94	0.31	0.14	1.04	0.38	52	76	27	78
7	C_6H_5O	C_6H_5O	108,5—109,5	0.03	1.4678	1.1023	−0.630	1.55	2.93	0.25	0.09	0.91	0.23	50	76	24	78
8	C_6H_5O	C_6H_5O	88—89	0.03	1.4654	1.0972	−0.822	1.65	3.14	0.20	0.05	0.58	0.12	38		11	
9	CH_3	C_6H_5O	72.5	1	1.4927	1.1809	−1.179	1.82	3.51					19	0	2	0
10	C_6H_5	C_6H_5	m.p. 141—142				−1.186	1.88	3.58					18		2	
11	CH_3	iso-C_3H_7O [1]	112—112,5	0.5	1.4819	1.0826	−1.205	1.91	3.69					16		1	
12	CH_3	C_6H_5O [1]	106—107	2.5	1.4883	1.1291	−1.280	1.87	3.78					15		1	
13	C_6H_5	C_6H_5O	84,5—85,5	2	1.4916	1.1330	−1.315	1.88	3.72					14	0	1	0
14	CH_3	C_6H_5O [1]	90	0.5	1.4891	1.0998	−1.370	1.95	3.77					12		0.8	
15	C_6H_5	C_6H_5O	101—102	2	1.4875	1.0974	−1.391	2.00	3.81					12	0	0.7	0
16	C_6H_5	C_6H_5O	64,5—65	0.015	1.4831	1.0721	−1.433	2.11	3.95					10	0	0.6	0
17	C_6H_5	C_6H_5O	110	1	1.4873	1.0810	−1.512	2.21	4.01					9		0.4	
18	iso-C_3H_7	C_6H_5O	82	0.1	1.4821	1.0321	−1.708	2.20	4.29					5		0.2	
19	C_6H_5	C_6H_5	88,5—89	1.5	1.5262	1.1090	−2.202	2.80	4.88					1		0.1	
20	C_6H_5	C_6H_5	98,5—99	2			−2.354	2.83	5.10					1		0	
21	C_6H_5	C_6H_5	84—84,5	0.25			−2.438	2.91	5.14					0.8		0	
22	iso-C_3H_7	iso-C_3H_7	m.p. 69,5—70,5				−2.504	3.17	5.46					0.5			
23	iso-C_3H_7	iso-C_3H_7	76—77,5				−2.600	3.03	5.46					0.5		0	
24	sec.-C_4H_9	sec.-C_4H_9	102—102,5	0.8			−2.726	3.10	5.71					0.4		0	
25	tert.-C_4H_9	tert.-C_4H_9	m.p. 144—145				−3.092	3.51	6.09					0		0	

[1] Sodium salt. [2] The measurements were inaccurate due to rapid hydrolysis of the CH_3O group. [3] Triethylammonium salt. [4] the pH of a solution of the triethylammonium salt was measured; the pK was calculated from the hydrolysis constants of the salt with an accuracy of ± 0.1 pK. [5] Calculations of the pK from the hydrolysis constant of the salt was difficult due to the unreliable value of K_W for 80% alcohol. [6] The substances were made available by N. N. Godovikov and E. I. Godyna.

the following results: for 7% alcohol $pK_T = 0.74 + 1.172 \Sigma\sigma$ when $r = 0.970$ and for 80% alcohol, when $r = 0.961$, $pK_T = 0.85 + 2.139 \Sigma\sigma$. Finally, the percentage contents of the thiol forms for solutions of all the substances investigated were calculated from the formulas obtained (see Table 1). For comparison, the results we had obtained previously by another method • are given beside them.

Thus, a quantitative analysis of a tautomeric equilibrium may be given on the basis of deviation of tautomeric acids from Hammett's linear relation of pK_a to σ (or $\Sigma\sigma$).

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• These data we obtained on the basis of a strict adherence to Bronsted's equation for organophosporus acids. In studying a large number of substances, we found that the slope of the lines $pK_{1S} = \alpha pK_{2S}$ + constant did not equal 45°. Therefore, these data are now changed somewhat.

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REACTION OF HEXAFLUOROBUTADIENE-1,3 WITH ALCOHOLS AND AMINES

Academician I. L. Knunyants, B. L. Dyatkin and L. S. German

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

The reactivity of 1,3-dienes of the perfluorocarbon series has hardly been studied. Only some radical reactions of hexafluorobutadiene-1,3, in which the conjugation effect of the double bond appears, are known. Thus, halogenation of it gives a mixture of 1,2- and 1,4-dihalides [1].

$$CF_2=CF-CF=CF_2 \xrightarrow{X_2} CF_2X-CF=CF-CF_2X + CF_2X-CFX-CF=CF_2.$$

and when heated, it is cyclized intramolecularly to hexafluorocyclobutene [2, 3]:

$$\begin{matrix} CF=CF_2 \\ | \\ CF=CF_2 \end{matrix} \longrightarrow \begin{matrix} CF-CF_2 \\ \| \quad | \\ CF-CF_2 \end{matrix}$$

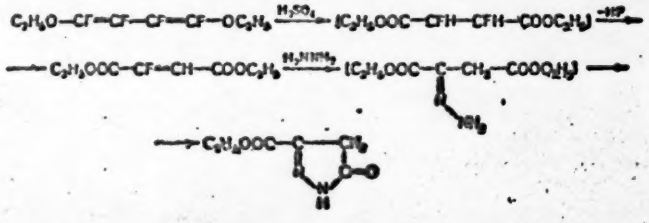
Reactions with nucleophilic reagents, which are so very characteristic of fluoroolefins, have not been investigated in the case of perfluorobutadiene. Meanwhile, it is these reactions especially which are most valuable in elucidating the nature of the conjugation of the bonds in perfluorinated dienes, since here, in contrast to diene hydrocarbons, there should be the transfer of a negative charge and not a positive charge along the conjugation chain:

$$A^{\ominus} + CF_2^{\delta-}-CF=CF-CF_2^{\delta+} \longrightarrow A-CF_2-CF=CF-CF_2^{\ominus}$$

By reacting perfluorobutadiene with sodium ethylate in ethanol, we obtained a substance which lost hydrogen fluoride when we attempted to isolate it in a pure form and gave 1,4-diethoxyperfluorobutadiene-1,3:

$$CF_2=CF-CF=CF_2 \xrightarrow[2.\ -HF]{1.\ C_2H_5ONa} C_2H_5O-CF=CF-CF=CF-OC_2H_5.$$

Treatment of the 1,4-diethoxyperfluorobutadiene-1,3 with concentrated sulfuric acid gave the diethyl ester of fluoroethylene-1,2-dicarboxylic acid, which reacted with hydrazine hydrate to form 3-carbethoxypyrazolone-5:



Thus, in the presence of an alcoholate, perfluorobutadiene reacts with two molecules of alcohol and the terminal carbon atoms are attacked nucleophilically.

When perfluorobutadiene was heated with alcohol in the presence of triethylamine, it added a molecule of alcohol. The results of a preliminary investigation of the reaction products (data on infrared spectra and nuclear magnetic resonance of F^{19}) indicated 1,4-addition:

$$CF_2=CF-CF=CF_2 \xrightarrow{ROH/(C_2H_5)_3N} RO-CF_2-CF=CF-CF_2H$$

$$R = CH_3;\ C_2H_5.$$

Perfluorobutadiene reacted with secondary and primary aliphatic amines under mild conditions. Reaction with diethylamine resulted in the formation of the unstable 1-diethylaminoperfluorobutadiene-1,3:

$$CF_2=CF-CF=CF_2 \xrightarrow{(C_2H_5)_2NH} CF_2=CF-CF=CF-N(C_2H_5)_2,$$

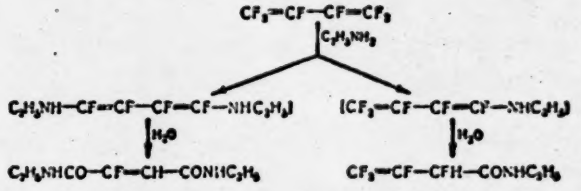
which was readily hydrolyzed to give the diethylamide of α-hydroperfluorovinylacetic acid:

$$CF_2=CF-CF=CF-N(C_2H_5)_2 \xrightarrow{H_2O} CF_2=CF-CFH-CON(C_2H_5)_2.$$

Perfluorobutadiene reacted with piperidine similarly:

$$CF_2=CF-CF=CF_2 \xrightarrow{C_5H_{10}NH} [CF_2=CF-CF=CF-NC_5H_{10}] \xrightarrow{H_2O} \rightarrow CF_2=CF-CFH-CONC_5H_{10}.$$

Reaction of perfluorobutadiene with ethylamine and hydrolysis of the reaction products gave the ethylamide of α-hydroperfluorovinylacetic acid and the bis-ethylamide of fluoroethylene-1,2-dicarboxylic acid:



In this case, as in the case of the ester, the bis-ethylamide of symmetric difluorosuccinic formed lost only one molecule of hydrogen fluoride and gave the corresponding derivative of fluoroethylene-1,2-dicarboxylic acid.

EXPERIMENTAL

1,4-Diethoxyperfluorobutadiene-1,3. With stirring and cooling in ice, 21 g (0.13 mole) of hexafluorobutadiene-1,3 was gradually added to a solution of sodium ethylate in ethyl alcohol, prepared from 4.8 g (0.21 g-at) of sodium and 200 ml of abs. ethanol. After a day the mixture was poured into dilute hydrochloric acid and the oil separated, washed with water and dried over calcium chloride. Decomposition with the evolution of hydrogen fluoride was observed. Distillation gave 18.9 g of a substance with b.p. 45-83°/17 mm. Several grams of powdered silica gel was added to this substance. The mixture heated up and hydrogen fluoride was evolved vigorously. The mixture was left overnight and then extracted with ether. The extract was washed with water and dried over calcium chloride. The residue after removal of the ether was vacuum distilled. We obtained 11.6 g (41.8% of theoretical) of 1,4-diethoxyperfluorobutadiene-1,3 with b.p. 83-87°/17 mm. A second distillation gave a substance with b.p. 83-85°/17 mm, $n^{20}D$ 1.3871, d^{20}_4 1.1883. MR found 42.44, calculated for $C_8F_4H_{10}O_2$ 42.05

Found %: C 44.41; H 5.06 $C_8F_4H_{10}O_2$. Calculated %: C 44.86; H 4.71

I. R. spectrum: ν_{max} 1740 cm^{-1}.*

* Here and in all subsequent cases, data on infrared spectra are presented for the range 1600-1900 cm^{-1}.

Diethyl ester of fluoroethylene-1,2-dicarboxylic acid. Over a period of 1.5-2 hours, about 2.5 ml of conc. sulfuric acid was gradually added to a solution of 9 g of 1,4-diethoxyperfluorobutadiene-1,3 in 20 ml of methylene chloride. The mixture was periodically shaken over a period of several hours, left overnight, then carefully washed with water and dried over magnesium sulfate. The methylene chloride was removed and the residue vacuum distilled. We obtained 6.7 g (83.6% of theoretical) of the diethyl ester of fluoroethylene-1,2-dicarboxylic acid, which distilled at 81-83°/3 mm. The compound had a pleasant, but at the same time irritating smell, reminiscent of the smell of diethyl acetylenedicarboxylate. A second distillation gave a substance with the following constants: b.p. 74°/1.5 mm, $n^{20}D$ 1.4330, d^{20}_4 1.1456. MR found 43.14, calculated for $C_8FH_{11}O_4$ F 41.84. E MR = 1.3

Found %: C 50.62; H 5.91; F 9.82 $C_8FH_{11}O_4$. Calculated %: C 50.52; H 5.83; F 9.99

1-Methoxyhydroperfluorobutene-2. A mixture of 16.2 g (0.1 mole) of hexafluorobutadiene-1,3, 6 ml of absolute methyl alcohol and 0.8 ml of triethylamine was heated at 90-100° for 4 hours in a steel tube of 75 ml capacity. The cooled mixture was decomposed with dilute hydrochloric acid and the oily layer separated, washed with water and dried over calcium chloride. As a result of distillation, we obtained 9.7 g (50% of theoretical) of 1-methoxy-4-hydroperfluorobutene-2 with b.p. 65-68°/748 mm. A second distillation gave a product with b.p. 30-31°/143 mm, $n^{20}D$ 1.3030, d^{20}_4 1.3696; MR found 27.37, calculated for $C_5F_6H_4O$ F 27.31

Found %: C 30.82; H 2.23; F 58.99 $C_5F_6H_4O$. Calculated %: C 30.94; H 2.08; F 58.74

I. R. spectrum: ν_{max} 1700(weak); 1730 cm^{-1}.

1-Ethoxy-4-hydroperfluorobutene-2. The reaction was similar to the one described above. From 14.5 g (0.09 mole) of hexafluorobutadiene-1,3, 10 ml of absolute ethyl alcohol and 1 ml of triethylamine, we obtained 10 g (53.5% of theoretical) of 1-ethoxy-4-hydroperfluorobutene-2, boiling at 48-51°/144 mm. As a result of a second distillation, we obtained a substance with the following constants: B.p. 49.5°/144 mm, $n^{20}D$ 1.3270, d^{20}_4 1.3090, MR found 32.17, calculated for $C_6F_6H_6O$ F MR 31.92.

Found %: C 34.85; H 3.03; F 54.77 $C_6F_6H_6O$. Calculated %: C 34.63; H 2.91; F 54.77

I. R. spectrum: ν_{max} 1730; 1790 (weak) cm^{-1}.

1-Diethylaminoperfluorobutadiene-1,3. With cooling with ice and vigorous stirring, 16.2 g (0.1 mole) of hexafluorobutadiene-1,3 was added over a period of half an hour to a solution of 18 g (0.25 mole) of diethylamine in 200 ml of absolute ether. Stirring and cooling were continued for a further hour and then the diethylamine hydrofluoride precipitate was filtered off and the ether distilled from the filtrate in vacuum at room temperature in a stream of nitrogen. Distillation of the residue yielded 17.4 g (81% of theoretical) of 1-diethylaminoperfluorobutadiene-1,3 with b.p. 45-50°/15 mm. A second distillation yielded a substance with b.p. 45°/15 mm, $n^{20}D$ 1.3960. Found: 9.29% of hydrolyzable F. Calculated for $C_8F_8H_{10}N$ (allowing for one hydrolyzable F atom) 8.83%. I. R. spectrum: ν_{max} 1710; 1800 cm^{-1}.

The diethylamide of α-hydroperfluorovinylacetic acid. A solution of 11 g of 1-diethylaminoperfluorobutadiene-1,3 in 20 ml of ether was shaken for several minutes with 25 ml of water, then the ether layer separated and dried with magnesium sulfate. The residue from removal of the ether was vacuum distilled. We obtained 9.4 g (86% of theoretical) of the diethylamide of α-hydroperfluorovinylacetic acid with b.p. 72-74°/5 mm. A second distillation gave a substance with the following constants: b.p. 63.5°/3.5 mm, $n^{20}D$ 1.4110, d^{20}_4 1.2428; MR found 42.63, calculated for $C_8F_4H_{11}NOF$ 43.06.

Found %: C 45.23; H 5.13; F 36.14; N 6.56 $C_8F_4H_{11}NO$. Calculated %: C 45.07; H 5.20; F 35.65 N 6.57

I. R. spectrum: ν_{max} 1660; 1800 cm^{-1}.

Piperidine of α-hydroperfluorovinylacetic acid. With cooling in ice and vigorous stirring, 12 g (0.075 mole) of hexafluorobutadiene-1,3 was added over a period of 45 minutes to a solution of 16 g (0.22 mole) of piperidine in 250 ml of abs. ether. Stirring was continued for a further 45 minutes at room temperature and then the mixture was decomposed with ice and dilute hydrochloric acid. The ether layer was separated and the aqueous one extracted with ether. The combined ether extracts were dried over magnesium sulfate, the ether removed and the residue vacuum distilled. We obtained 8 g (48% of theoretical) of the piperidine of α-hydroper-

fluorovinylacetic acid as a colorless, immobile liquid with b.p. 92-95°/4 mm. A second distillation gave a substance with b.p. 94°/5 mm, $n^{20}D$ 1.4420, d^{20}_4 1.3203; MR found 45.13; calculated for $C_5F_4H_{11}NOF$ 45.48.

Found %: C 48.16; H 4.71; F 34.00 $C_5F_4H_{11}NO$. Calculated %: C 48.00 H 4.92; F 33.75

I. R. spectrum: ν_{max} 1660; 1800 cm^{-1}.

Reaction of hexafluorobutadiene-1,3 with ethylamine. With stirring and cooling in ice and salt mixture, 16 g of hexafluorobutadiene-1,3 was added over a period of half an hour to a solution of 20 ml of ethylamine in 150 ml of abs. ether. Stirring was continued for a further 15 minutes with cooling and 30 minutes at room temperature. Then the reaction mixture was decomposed with ice and dilute hydrochloric acid, the ether layer separated and the aqueous one extracted with ether. The combined ether extracts were left overnight, then the crystals of the bis-ethylamide of fluoroethylene-1,2-dicarboxylic acid (4.5 g) which separated were filtered off and recrystallized from water. The m.p. was 195°.

Found %: C 51.10; H 6.87; F 10.06; N 14.94 $C_8FH_{11}N_2O_2$. Calculated %: C 51.05; H 6.96; F 10.10 N 14.89.

The ether was distilled from the filtrate in vacuum. We obtained 0.7 g of a crystalline residue, which was the ethylamide of α-hydroperfluorovinylacetic acid. The m.p. was 55-56° (from n-octane).

Found %: C 38.56; H 3.86; N 7.59 $C_6F_4H_7NO$. Calculated %: C 38.92; H 3.81; N 7.56

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POLAROGRAPHY OF COPPER α-ALANINATE

E. A. Maksimyuk and G. S. Ginzburg

I. P. Pavlov First Medical Institute, Leningrad

(Presented by Academician A. A. Grinberg, October 20, 1958)

In papers published previously [1, 2] it was shown that in the case of a retarded stage of discharge of a complex, the specific adsorption of the addend displaced the half-wave potential at a mercury dropping electrode in a direction determined by the sign of the ion charge and by the value of the adsorption potential, and also that the specific adsorption of the discharged ion itself led to a sharp displacement of the half-wave potential toward the positive side. Cis- and trans-isomers show different tendencies for specific adsorption and due to this, it is possible to identify these isomers by the value of the half-wave potential. It is true that such a difference is observed only in neutral molecules and monovalent ions. No difference in the values of the half-wave potentials of the cis- and trans-isomers of the trivalent ion $[Co\ en_2(NH_3)_2]^{3+}$ could be found, as in this case the charge of ion (3+) suppressed the effect of the polarity of the ion.

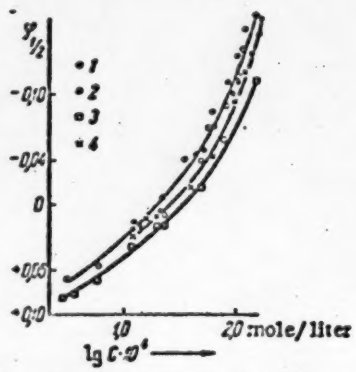

Fig. 1. The relation of the half-wave potential to salt concentration.
1) Needle form of copper glycolate; 2) plate form of copper glycolate; 3) needle form of copper α-alaninate; 4) plate form of copper α-alaninate.

A. A. Grinberg and Z. E. Gol'braikh [3] thoroughly studied the properties of the needle-like and the plate-like forms of copper glycolate. An attempt to explain the existence in the crystal structure of two forms of copper glycolate by the presence of cis- and trans-isomerism, was unsuccessful in contrast to what was established by A. A. Grinberg and B. V. Pitysn [4] in the case of the needle-like forms of the glycolate of divalent platinum. We also found no difference in the half-wave potentials when plotting polarograms of the needle and plate forms of copper glycolate in solutions of various concentrations. Thus, up to now, no difference has been found between the needle and plate forms of copper glycolate in aqueous solution.

In 1956 Z. E. Gol'braikh was the first to prepare the plate form of copper α-alaninate [5]. Z. E. Gol'braikh tried to establish the difference between the structures of the needle and the plate forms of copper α-alaninate, but, having put forward a hypothesis on the existence of cis- and trans-isomerism, found no proof of it.

In the present work, the character of the reduction of the two forms of copper α-alaninate at a mercury dropping electrode was studied. The appropriate different forms of copper α-alaninate were prepared by Z. E. Gol'braikh's method [5]. The material being investigated was dissolved in a 0.1 N solution of potassium sulfate, which acted as the base. Gelatin was used to suppress the maxima. A mercurous sulfate electrode was used as the anode.

Figure 1 shows that the half-wave potentials of the needle and plate forms of the α-alaninate have different values. The half-wave potentials of the needle crystals of the α-alaninate are more positive than the half-wave potentials of the plate crystals. It is impossible to assign a cis- or trans-structure unequivocally to one or other form on the basis of the polarographic method, but the existence of other data on the possibility of cis- and

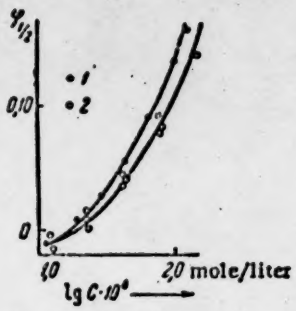

Fig. 2. The relation of the half-wave potential to concentration of copper glycolate at 20° (1) and at 50° (2).

trans-isomerism in the forms of copper α-alaninate being studied indicates that a cis-structure may be assigned to the needle form.

The stability of copper glycolate and α-alaninate are practically the same.

The mean values of the negative logarithms of the instability constants, obtained by various methods, are equal to 15.3 for copper glycolate and 15.2 for copper α-alaninate [6].

It follows from Fig. 1 that the half-wave potentials of copper glycolate have a more negative value and, consequently, having the same stability, copper glycolate has a lower specific adsorption than the α-alaninate.

The results obtained refer to a temperature of 20°.

As Fig. 2 shows, at 50° the half-wave potentials of the needle and plate forms of copper glycolate in the region of low concentrations coincide with the half-wave potentials at 20° and at higher concentrations, the half-wave potentials at 50° are displaced toward the positive side. The plate form of copper α-alaninate behaves similarly. However, as regards the needle form of copper α-alaninate, the curves of the relation of the half-wave potential to concentration at 20° and 50° coincide along their whole length.

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A HIGHER HYDRATE OF FERRIC OXIDE

P. S. Meleshko

I. V. Stalin State Medical Institute of the Crimea, Simferopol

(Presented by Academician I. I. Chernyaev, October 25, 1958)

The extensive literature devoted to the problem of the composition of colloidal ferric hydroxide includes many references to the existence of higher hydrate forms (containing three to nine water molecules per two molecules per two molecules of ferric oxide). However, a critical examination of the results of various authors' investigations makes the majority of the data obtained questionable due to the inadequacy of the methods used. In the first case, this refers to those works in which use was made of old methods of preparative chemistry that are unsuitable for investigating colloidally dispersed systems [1-4]. The same may be said of the investigations in which the authors used methods of physicochemical analysis that are applicable in the analysis of coarsely crystalline phases and did not take into consideration the specific characteristics of colloidally dispersed systems when applying these methods to a study in this field [5-10].

TABLE 1

The $Fe_2O_3 - H_2O - NH_4Cl$ System

Sample No.	Liquid phase	Mixture of liquid and solid phases (LS), %	
	NH_4Cl, % (c)	Fe_2O_3 (a)	NH_4Cl (b)
I	3.95	22.96	3.27
II	7.90	21.65	6.44
III	11.52	22.75	9.08
IV	15.30	21.61	12.02
V	18.48	19.30	14.55

The "third component" method proposed by P. T. Danil'chenko [11] makes it possible to determine unequivocally the amount of water bound chemically in a colloidal hydrate. Analysis of an aged ferric hydroxide gel by the method of P. T. Danil'chenko showed that it was the monohydrate $Fe_2O_3 \cdot H_2O$ [12]. Investigation of freshly precipitated preparations of colloidal ferric hydroxide [13, 14] indicated the presence of hydrates with the composition $2Fe_2O_3 \cdot 5H_2O$, $Fe_2O_3 \cdot 2H_2O$ and $2Fe_2O_3 \cdot 3H_2O$, which were unstable compounds that dehydrated at normal temperature to stable monohydrates. Although in textbooks the formula of ferric hydroxide has been given as $Fe(OH)_3$ ($Fe_2O_3 \cdot 3H_2O$) for a long time, the existence of such a hydrate could not be proven up to now. One must admit that the reason for this is the extreme instability of the trihydrate, but under the known preparation conditions it is still practicable.

To prevent the decomposition of freshly prepared colloidal ferric hydroxide, it was necessary to lower as far as possible the temperature for the preparation and investigation of the hydrogel and to cut down the time

from the moment that the preparation was formed to its analysis and therefore the investigation procedure used [13] was modified. The ferric hydroxide gel was obtained by pouring a definite volume of a 1 N solution of $FeCl_3$ into an equal volume of a 2 N solution of ammonia. The concentrations of the two solutions were rigidly set. Then a calculated amount of 0.2 N HCl titration solution was added (with vigorous stirring) to the reaction flask until the excess ammonia was completely neutralized. Having used ammonium chloride as the third component, we did not need to wash the preparation (which usually required at least 20 days).

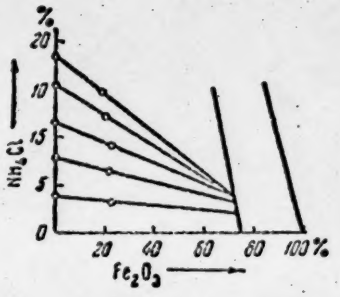

Fig. 1

The hydrogel was precipitated at an air temperature of not more than 2° (the reaction flask was placed in snow and the reacting solutions were cooled first to 1°). Five portions of hydrogel, filtered and condensed in the cold, were placed in test tubes with cooled solutions of NH_4Cl at various concentrations (from 5 to 25%). The test tubes were placed in a beaker with snow and transferred to a refrigerator, where the temperature was below 2°. Silver wire stirrers had been threaded through the stoppers of all tubes and these were used to mix the contents of the tubes carefully several times per day. After the adsorption equilibrium had been established, on the sixth day after the preparation of the gel, portions of the equilibrium solution and of the mixture of the solid and liquid phases were collected for analysis.

The results of investigating the $Fe_2O_3 - H_2O - NH_4Cl$ system are shown in Table 1 and are plotted on a triangular diagram ([11], see also Fig. 1).

As the diagram shows, the three lines of the composition of the LS mixture, corresponding to the highest concentrations of the equilibrium solutions, intersect at one point. The "hypotenuse of the hydrate composition" drawn through this point intersects the abscissa at the percentage ratio $Fe_2O_3/H_2O = 75/25$, which corresponds to the hydrate $Fe_2O_3 \cdot 3H_2O$ (calculated 74.71% of Fe_2O_3).

To obtain more accurate data, the composition of the hydrate was also calculated [11, 13]. The diagram shows that in tubes I and II, the maximum adsorption of the dissolved material on the surface of the hydrogel was not achieved and therefore the analysis data for these samples were not used in calculating the composition of the hydrate. In order to find the content of the anhydrous substance in the hydrate, x, the values c' and c", a' and a" and b' and b", corresponding to the three pairs of samples: III and IV, III and V, and IV and V, were substituted alternately in the equation.

$$x = \frac{a'a''c''(100 - c') - a'a''c'(100 - c'')}{a'(100 - c')(c'' - b'') - c''(100 - c')(c' - b'')}$$

The values obtained are: $x_{III-IV} = 75.64$; $x_{III-V} = 75.06$; $x_{IV-V} = 74.41$. The average of the three values equals 75.04%.

Thus, the analytical data agree well with those obtained graphically. If one considers the unavoidable experimental errors, then the presence of ferric hydroxide trihydrate may be considered as proven and the conditions for its existence also established. This supplements our knowledge of the higher hydrates of ferric oxide. The investigation procedure used widens the possibility of studying freshly precipitated colloidal hydrates.

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PREPARATION OF KETONES CONTAINING AN ATOM OF TIN IN A POSITION α TO THE CARBONYL GROUP

Academician A. N. Nesmeyanov, I. F. Lutsenko and S. V. Ponomarev

M. V. Lomonosov Moscow State University

Continuing the investigation of the simplest metal enolates [1], we tried to prepare them by an exchange reaction between metal alcoholates and acetates of enol forms. In this article we give the results of studying the reaction of enol acetates with trialkylmethoxystannanes.

Mixing equivalent amounts of R_3SnOCH_3 and an enol acetate resulted in moderate heat evolution and the alkyl acetate (quantitatively) and an organotin compound (70-95% yield) could be distilled from the reaction mixture. A detailed study of the organotin derivatives thus obtained showed that they were not the enolates of trialkyltin, but α-metallated ketones, isomeric with them.

The problem of whether the organotin compound, obtained from isopropenyl acetate and R_3SnOCH_3 had the ketone structure $R_3SnCH_2COCH_3$ (I) or the enolate structure $R_3SnOC(CH_3)=CH_2$ (II), could be solved spectroscopically – by investigating the infrared and Raman spectra in two regions: in the region 1600-1700 cm^{-1}, which includes the oscillation bands of the C=C and the C=O bonds and in the region ~3000 cm^{-1}, which includes the bands of the valence oscillation of C–H.

The infrared spectra of the organotin compounds obtained showed intense absorption at 1684 cm^{-1} ($R=C_4H_9$) and at 1686 cm^{-1} ($R=C_2H_5$).* Aliphatic ketones have characteristic bands in the region 1700-1725 cm^{-1}. However, when a double bond or an aromatic ring, conjugated with the C=O group, is present in a molecule, the oscillation frequency of the ketone carbonyl group drops 1665-1685 cm^{-1}. Compounds with structure (I) have in the position α to the carbonyl group an atom of tin with a relatively high polarizability, which should induce a decrease in the frequencies of the oscillations, similar to the effect produced by a double bond or an aromatic ring, and this was actually observed. It should be noted that in the case of α-mercurated ketones, an even greater displacement is observed and the absorption bands of the 6 mercury ketones investigated lay at 1660-1670 cm^{-1}.

A band at 1671 cm^{-1} was found in the Raman spectrum of the organotin compounds synthesized.

The frequency values obtained are too high for the C=C bond (structure (II)). The lithium vinylate we described previously [1] had an absorption band in the infrared spectrum, corresponding to the oscillations of the double bond, at 1610 cm^{-1}. Furthermore, no absorption bands could be found in the region ~3040-3090 cm^{-1} as would be expected with structure (II), either in the infrared or in the Raman spectra. Finally, as in the case of mercurated aldehydes and ketones, the organotin compounds obtained had ultraviolet absorption spectra with intense bands in the absorption region of carbonyl compounds and there was a slight displacement of the characteristic band toward the long wavelength region as compared with that of acetone and a very strong increase in intensity: CH_3COCH_3 λ_{max} 271 mμ, lg ε 1.2; $ClHgCH_2COCH_3$ λ_{max} 296 mμ, lg ε 2.50; $(C_2H_5)_3SnCH_2COCH_3$ λ_{max} 277-280 mμ, lg ε 2.34; $(C_4H_9)_3SnCH_2COCH_3$ λ_{max} 281-283 mμ, lg ε 2.10. These spectroscopic data allow

* We would like to take this opportunity to thank L. A. Kazitsyna, E. G. Treshchova and B. V. Lokshin, who carried out the spectroscopic investigation of triethylacetonyltin and tributylacetonyltin.

us to assign the structure of α-metallated ketones to the organotin compounds we synthesized. A thorough spectroscopic investigation was carried out as the extreme hydrolyzability of the compounds obtained made it difficult to solve the problem of structure by chemical methods.

The reaction between R_3SnOCH_3 and enol acetates proceeded by the following summarized equation:

$$R_3SnOCH_3 + CH_2{=}C(OCOCH_3){-}CH_3 \rightarrow CH_3COCH_2SnR_3 + CH_3COOCH_3.$$

and may be examined formally as the addition of the organotin compound at the double bond. The constants, yields and analyses of the organotin ketones are given in Table 1.

TABLE 1

Compound	Yield, %	B. p.	n_D^{20}	d_4^{20}	Calc. C	Calc. H	Calc. Sn	Found C	Found H	Found Sn
$(C_2H_5)_3SnCH_2COCH_3$	95	100,5—101°/6 mm	1,4991	1,2875	41,12	7,61	45,21	41,45 41,29	7,85 7,77	
$(C_2H_5)_3Sn$-(cyclohexanone)	72	116—117°/4 mm	1,5057	1,2872	47,56	7,98		47,57 47,69	7,55 7,81	
$(C_3H_7)_3SnCH_2COCH_3$	78	98—100°/1 mm	1,4865	1,1983	47,25	8,58	33,90	47,16 47,26	8,70 8,62	
$(C_4H_9)_3SnCH_2COCH_3$	85	130—122°/2 mm	1,4842	1,1255	51,92	9,29	34,21	52,05 52,17	9,56 9,64	34,39 34,39
$(C_4H_9)_3Sn$-(cyclohexanone)	70	155—156°/1 mm	1,4805	1,1290	55,85	9,31	30,70	55,25	9,51	31,09

The new class of metalloorganic ketones, containing an atom of tin in the α-position, have very different properties from those of ketones containing an R_3Sn group in the β-position [2]. Thus, triethylacetonyltin was readily and rapidly hydrolyzed in water (with noticeable heat evolution) to give triethyltin hydroxide and acetone. Such an unexpectedly easy hydrolysis of the C—Sn bond doubtlessly is caused by the presence of σ-π-conjugation in the molecule of the compound. In particular, this conjugation effect is also seen in the displacement of the oscillation frequencies in the UV and IR spectra, both in organomercury and organotin oxo compounds. Our attempts to prepare metallated acetaldehyde from vinyl acetate and R_3SnOCH_3 ($R = C_2H_5, C_4H_9$) have so far been unsuccessful. Although on mixing equivalent amounts of vinyl acetate and R_3SnOCH_3, the reaction mixture heated up noticeably and methyl acetate could be distilled quantitatively from it, the expected R_3SnCH_2CHO decomposed during vacuum distillation (with a residual pressure of 1-1.5 mm).

In connection with this, we would like to note the recent report of M. Lesbre and Buisson [3], in which they describe the preparation of tributylacetonyltin from tributylstannane and diazoacetone. This compound is described as a thick, yellow liquid with b.p. 130-134°/14 mm. No other characteristics, not even carbon and hydrogen analyses, are given while the tin analysis differs from the calculated value by more than 1%.

The sample of tributylacetonyltin we prepared and characterized by complete analysis and IR and UV spectra is a colorless liquid with b.p. 130-132°/2 mm. Distillation of the compound at higher pressure (4-5 mm) resulted in noticeable decomposition of the substance, which distilled in the form of a yellow liquid under these conditions. These data, as well as the considerable difference in boiling points, seem to indicate that M. Lesbre obtained and described an impure compound.

The starting trialkylmethoxystannanes were prepared in 70-80% yields from trialkylchlorostannanes and sodium methylate in absolute methyl alcohol.

$(C_2H_5)_3SnOCH_3$, b.p. 73-74°/13 mm; $n^{20}D$ 1.4760, d^{20}_4 1.3065; $(C_3H_7)SnOCH_3$, b.p. 87-88°/3 mm, $n^{20}D$ ..., d^{20}_4 ..., $(C_4H_9)_3SnOCH_3$, b.p. 101-102°/2 mm, $n^{20}D$ 1.4745, d^{20}_4 1.1690.

Preparation of triethylacetonyltin. 5 g (0.05 mole) of isopropenyl acetate was added to 11.8 g (0.05 mole) of triethylmethoxytin. The reaction mixture heated up noticeably. The mixture was heated for half an hour and then the methyl acetate distilled off at 40-50°. The residue was vacuum distilled and the substance obtained had b.p. 100.5-101°/6 mm and the yield was 12.3 g (95% of theoretical). The other compounds were prepared similarly.

Reaction of triethylacetonyltin with water. 0.2 g of water was added to 2.6 g (0.01 mole) of triethylacetonyltin. After 1 minute the mixture gave off heat and crystallized completely to triethyltin hydroxide with m.p. 44°.

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THE EFFECT OF COMPOSITION AND CONDITIONS OF HEAT TREATMENT ON THE STRUCTURE AND CATALYTIC ACTIVITY OF $Al_2O_3 - ZrO_2$ CATALYSTS

A. M. Rubinshtein, V. A. Afanas'ev, V. M. Akimov, N. A. Pribytkova and K. I. Slovetskaia

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

(Presented by Academician A. A. Balandin, October 17, 1958)

This investigation is a development of our study of binary catalysts based on Al_2O_3 [1,2]. ZrO_2 is used as an additive to or a component of mixed catalysts, but we have not encountered works which either describe the results of systematically changing the ratio of components and the conditions of heat treatment or determine the specific activity of such catalysts. The structure of the $Al_2O_3 - ZrO_2$ system is studied in article [3] in which the effect of mutual protection from crystallization of the components is examined and in article [4] which contains a detailed x-ray structural description of such preparations.

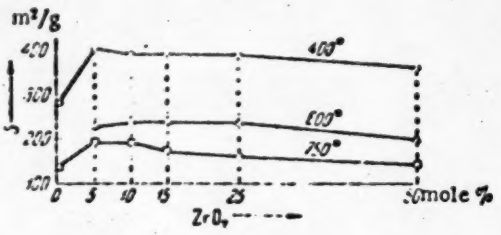

Fig. 1

We investigated the decomposition of absolute isopropyl alcohol on $Al_2O_3 - ZrO_2$ catalysts, prepared by coprecipitation from volumes of 10% solutions of Al and Zr nitrates in appropriate ratios, with 10% ammonia, at room temperature and with a final pH of 8.7-9.5. The washed and molded precipitates were dried at 110° and separate portions of each preparation were fired at 400, 600, and 750°. The water loss was determined; it was found that even at 400° the dehydration of the hydroxides was quite high and that the catalysts consisted of oxides. Raising the firing temperature to 750° eliminated only an additional 2% of the water present in an adsorbed state in catalysts that had been fired at 400°. The prepared, fired catalysts were grains with a cross section of 1.2-1.3 mm. In the main experiments 3 cm of catalyst was loaded into the reactor. $i\text{-}C_3H_7OH$ was decomposed in a flow system [1] with a volume rate of 1.0 hr^{-1} and the activity was determined by the volume and composition of the gas evolved. The values of the reaction rate constants K were calculated from the experimental data by the equation $K = Nm/(M - m/2)$ [5] and the specific activity A_{spec} was calculated from the values K and S (specific surface) (Table 1). The values of S were obtained by measuring the adsorption isotherms of benzene vapor at 20° by a dynamic method [6] and calculating by the BET equation. The corresponding data are given in Fig. 1, which shows that the catalysts investigated had a very highly developed surface and were quite heat stable as their surface was found to be extremely great even after firing at 750°. This indicates the mutual protective effect from crystallization (sintering) of the components of the catalysts. The change in the porous structure of the catalysts when fired may be seen in Fig. 2, which gives the curves of diameter distribution of the pores, calculated by Kelvin's equation, for catalysts with 10 mole % ZrO_2; the curves show a displacement and a widening of the maximum with an increase in the firing temperature. This picture is typical of the changes occurring during heat treatment of catalysts of the system investigated.

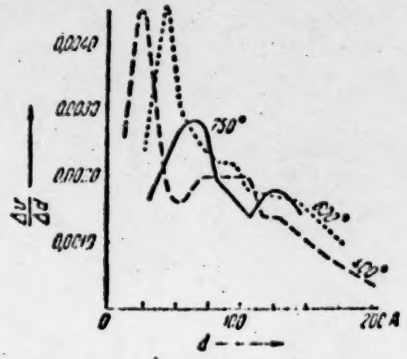

Fig. 2

$Al_2O_3 - ZrO_2$ catalysts were active even at 250° while ZrO_2 had the same activity only at 300°. To save space, in Table 1 we give the degree of change, characterizing the general activity only at temperatures of 245 and 260°. Under these conditions only the dehydration of $i\text{-}C_3H_7OH$ occurred on all the binary catalysts. Examination of the data in Table 1 shows that the addition of 5 mole % ZrO_2 to catalysts fired at 400° did not increase the general activity and the addition of 10 mole % and more increased it little. The increase in activity is definitely due to considerably greater values of S of binary catalysts in comparison with Al_2O_3. The same results were obtained in comparing the general activity of Al_2O_3 and of binary catalysts, fired at 750°; at first, in spite of the greater value of S, binary catalysts are less active than Al_2O_3, and only starting with 15 mole % of ZrO_2 do they become as active. We can thus conclude that under these conditions Al_2O_3 is not activated by the addition of ZrO_2.

Figure 3 gives a graph of the changes in A_{spec} with composition and catalyst firing temperature (1 – 750°, 2 – 600°, 3 – 400°) in experiments at 260°; a similar picture was obtained for experiments at 245 and 230°, although in these cases there was some scattering of points in the region of 5-15 mole % of ZrO_2. Fig. 3 shows that from 5 to 15 mole % of ZrO_2 A_{spec} grows and then does not change with composition: starting of 15 mole % of ZrO_2, for various firing temperatures A_{spec} forms a system of lines which are parallel to the concentration axis. The constancy of A_{spec} over wide range of ZrO_2 concentrations indicates that under these conditions the reaction proceeds only on Al_2O_3 and that the ZrO_2 acts only as an inert carrier. As can be seen from the data in Table 1 (S and the degree of conversion) and Fig. 3, A_{spec} of pure Al_2O_3 is greater than the A_{spec} of binary catalysts; a more detailed study of the A_{spec} of Al_2O_3 showed that at 245° it equalled $2.25\text{-}2.58 \cdot 10^{-4}$ mole/m^2·min, i.e. was of the same order as the A_{spec} of binary catalysts at 260°. All this agrees well with the data from x-ray analysis of the catalysts (in which L. D. Kretalova also participated), carried out with RKD cameras by an asymmetric method using CuKα radiation with an Ni filter. The phases were identified from tabulated data for the pure components [4] and by comparison with the x-ray photos of the pure components prepared under the same conditions. The x-ray photos of the binary catalysts fired at 400° contained reflections of $\gamma\text{-}Al_2O_3$ which weakened with an increase in the ZrO_2 concentration, which, apparently, is amorphous in this series of catalysts. The ZrO_2 x-ray (400°) had very strong lines of tetragonal and very weak ones of monoclinic ZrO_2. The series obtained at 600° gave a similar picture for the binary catalysts except that weak lines of the tetragonal modification of ZrO_2 appeared in the x-ray photo of the catalyst with 47 mole % of ZrO_2; pure ZrO_2 was found to be monoclinic with some tetragonal form. Starting with 10 mole % of ZrO_2 the catalysts of the 750° series gave x-rays which had lines of tetragonal ZrO_2 besides the $\gamma\text{-}Al_2O_3$ lines; in this series the pure ZrO_2 was of a monoclinic form with only traces of the tetragonal form. We thus

TABLE 1

Experimental Data Obtained with $Al_2O_3 - ZrO_2$ Catalysts

ZrO_2 content, mole %	$pH_{precip.}$	Heat treatment, °C	Bulk weight, g/cc	S, m^2/g	Degree of conversion $i\text{-}C_3H_7OH$, %	
					245°	260°
0*	8,5	400	—	284	—	77
5	8,7	400	0,76	403	33	76
10	8,9	400	0,71	392	39	82
15	9,0	400	0,71	396	48	84
25	9,2	400	0,76	393	55	89
50 (47)	9,5	400	0,85	362	47	88
100	9,0	400	1,3	120	—	42**
5		600	0,73	250	69	91
10		600	0,70	241	53	86
15		600	0,69	240	54	92
25		600	0,76	236	76	95
50		600	0,86	198	72	90
100		600	1,3	41	—	45***
0		750	—	135	—	88
5		750	0,72	196	45	70
10		750	0,70	191	37	75
15		750	0,69	171	47	85
25		750	0,79	160	72	93
50		750	0,86	143	58	91
100		750	1,4	13	—	31***

* Pure Al_2O_3.

** At 300°, including 1% dehydrogenation.

*** At 320°, including 3% dehydrogenation.

established that in catalysts prepared by coprecipitation, ZrO_2 and Al_2O_3 in the form of independent phases and do not form solid solutions (as follows from a calculation of the lattice parameters). This agrees with the data of Ruff and Ebert [4], who found that up to 1800° ZrO_2 and Al_2O_3 do not react to form solid solutions.

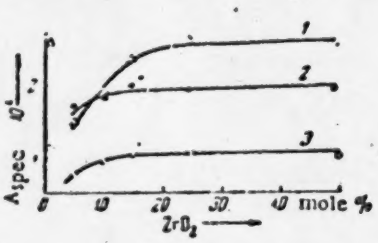

Fig. 3

We carried out additional experiments at 320° with catalysts fired at 600°, as under these conditions the activity of pure ZrO_2 is considerable. This required an increase in the volume rate to 12 hr^{-1}. We obtained the following values in these experiments: $A_{spec} \cdot 10^4 = 17$; 15; 23; 23 and 25 at 5; 10; 25 and 47 mole % of ZrO_2, respectively; under these conditions only dehydration of the alcohol occurred while on pure ZrO_2, dehydrogenation also occurred. The data given show that an increase in temperature and volume rate did not change the general picture shown by Fig. 3 nor did it affect the conclusions drawn from Fig. 3 and Table 1.

The increase in general activity in the range 400-600° (Table 1) and in A_{spec} with firing temperatures (Fig. 3) may be explained by the destruction of the finest pores, which are difficultly accessible to the alcohol, found in catalysts of the 400° series and also, though to a lesser degree, in catalysts fired at 600°, as the fraction of S due to them enters the calculation of A_{spec}.

In conclusion we should note that the x-ray structural data we obtained indicate that γ-Al_2O_3 stabilized the tetragonal form of ZrO_2 and considerably increased the temperature of its phase conversion to the monoclinic form.

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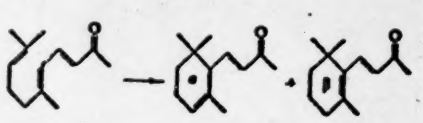
THE CHARACTER OF THE CYCLIZATION OF PSEUDOIONONE

V. A. Smit, A. V. Semenovskii, V. M. Medvedeva and V. F. Kucherov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

(Presented by Academician B. A. Kazanskii, October 30, 1958)

A large number of experimental investigations have been devoted to the study of the cyclization conditions of pseudoionone [1-8] and these works showed that pseudoionone is converted into a mixture of α- and β-ionones under the action of various acids. The ratio of the α- and β-isomers formed depends to a considerable degree on the nature of the cyclizing agent. It is now generally accepted that the specific cyclizing agent for the preparation of β-ionone is concentrated sulfuric acid in ether or acetic acid, while for the preparation of α-ionone one must use 60% sulfuric or phosphoric acids or, best of all, boron trifluoride.



However, analysis of the large amount of literature on the cyclization of various isoprenoid compounds indicate that regardless of the nature of the agent, in almost all cases the first reaction product is the α-isomer [9-13], which is converted by the further action of acid agents into the more stably conjugated system of the β-isomer [14, 15]. According to this, the specific character of the action of different cyclizing agents must reduce to only a greater or smaller extent the capacity for the isomerization of the initally formed isomer.

In order to confirm this premise experimentally, we studied the cyclization of pseudoionone under the action of sulfuric acid at different temperatures (from +60 to −60°). The cyclizing agent used was 100% sulfuric acid as this gave a smaller amount of side products. In all the experiments, the solvent used was nitromethane or nitropropane, which have low freezing points and dissolve sulfuric acid well. The standard procedure for the experiment consisted of the following: 10 g of pseudoionone was added with stirring to a solution of 15 ml of sulfuric acid in 20 ml of nitromethane. The reaction temperature during the addition and the subsequent standing period was regulated by external cooling. The reaction mixture (a red, homogeneous liquid) was poured into a mixture of 200 ml of ice water and 150 ml of petroleum ether with stirring. After extraction, washing with sodium bicarbonate solution, drying and removal of the solvent, the residue was separated from tarry material by vacuum distillation. Without further purification, the distillate was analyzed for α- and β-ionone contents by the UV spectrum.* The amount of β-isomer was determined by the intensity of its characteristic absorption maximum at 298 mμ (ε = 10700) and the amount of the α-isomer by the absorption intensity in the region 225-227 mμ (ε = 14200) with an allowance for the small absorption of β-ionone in this region (ε = 6500). As was demonstrated by analysis of authentic mixtures, the error in determining the amount of the isomeric ionones by this method did not exceed ± 2%. In separate cases, the purity of the α- and β-ionones formed was confirmed as far as possible by the quantitative isolation of their crystalline derivatives.

* The spectra were plotted with the help of T. M. Fadeeva.

The results obtained are presented in Table. 1. As these data show, the ratio of the α- and β-ionones formed is completely determined by the cyclization conditions, i. e., time, temperature and amount of sulfuric acid. When the reaction was performed at −60°, a product was obtained which contained hardly any β-ionone,

TABLE 1

Expt. no.	H_2SO_4, moles/mole of pseudoionone	Temp., °C	Time, min	Yield of distilled product, %	UV spectra, ε		Content of mixture, %	
					λ = 226 mμ	λ = 296 mμ	α-Ionone	β-Ionone
1	6:1	+10	3	70	6375	10160	5	95
2		0	2	73	8050	8800	19	82
3		From −35 to −40	3	90	12500	2980	72	28
4			300	72	6330	9550	4	89
5*		−60	60	75	13200	1700	86	16
6	2:1	+10	3	85	10690	4050	59	38
7		−30	4	80	13400	1730	83	16
8		−30	180	80	12420	2130	79	20
9	1:1	+10	3	83	11050	2780	67	26
10		0	5	73	—	—	Cyclization was incomplete	
11		−10	50	80	10800	2610	66	24
12	0,4:1	+10	3	83	—	—	Pseudoionone recovered completely	
13		+30	3	78	—	—	Cyclization was incomplete	
14		+60	2	62	7350	2880	48	27
15	11:1	−40	5	83	12810	2070	82	19
16**	95% H	+10	1	85	6000	6400	15	60
17**		−40	1	83	13250	1740	87	16

* Experiment in nitropropane.
** 95% H_2SO_4.

TABLE 2

Expt. no.	H_2SO_4, moles/mole of α-ionone	Temp. °C	Time, min	Yield of distilled product, %	UV spectra, ε		Content in mixture, %	
					λ = 226 mμ	λ = 296 mμ	α-Ionone	β-Ionone
1	6:1	+10	2	82	7800	8500	18	80
2		0	30	90	8420	7090	29	66
3		−40	5	95	11700	2400	73	22
4		−40	70	85	8400	7410	28	69
5		−40	180	95	6320	9250	4	87
6		−60	600	86	12600	880	87	8
7	2:1	−30	180	90	13290	1310	89	12
8	1:1	+10	3	82	13400	1100	91	10
9	4:1*	+40	10	88	14300	—	100	—
10	4:1**	+40	120	92	13800	—	100	—

* 60% H_2SO_4.
** 85% H_3PO_4.

even with prolonged reaction (Expt. No. 5). With the same amount of sulfuric acid (6 moles per mole of pseudoionone) and at −40°, depending on the reaction time, it is possible to prepare mixtures with a predominance of α-ionone (Expt. No. 3) or β-ionone (Expt. No. 4), while the reaction can be carried out successfully at the same temperature with 95% sulfuric acid (Expt. No. 17). With an increase in the cyclization temperature, there

is a sharp increase in the amount of β-ionone formed and at +10° there is hardly any α-ionone in the mixture formed even with the minimal reaction time (Expt. No. 1).

The ratio of the α- and β-isomers can also be changed by varying the amount of the cyclizing agent. Thus, when the amount of sulfuric acid is reduced to 1 mole per mole of pseudoionone, even at +10° the cyclization product contains up to 67% of α-ionone (Expt. No. 9). A further reduction in the amount of sulfuric acid (to 0.4 mole) leads to the formation of mixtures with a predominance of α-ionone, even +60°(Expt. No. 14). An increase in the amount of sulfuric acid (to 11 moles) does not lead to a significant changes in the ratio of α- and β-isomers at −40°(Expt. No. 15).

Examination of the results above shows that the initial and the basic reaction product of pseudoionone cyclization is α-ionone. This was confirmed by a study of the conditions of its isomerization into β-ionone (Table 2). As would be expected, complete agreement was observed between the yields of β-ionone during cyclization and the degree of isomerization of α-ionone into the β-isomer under identical reaction conditions.

The isomerization of α-ionone into β-ionone proceeds rapidly and completely at elevated temperatures (Expt. No. 1 and 2) and requires a considerable time for completion at low temperatures (Expt. No. 4 and 5). It is interesting that at −60° it is possible to almost completely exclude this isomerization (Expt. No. 6), while the cyclization proceeds quite rapidly at this temperature. A decrease in the amount of acid to 1 mole per mole of α-ionone supresses the isomerization, even at +10°(Expt. No. 8). Phosphoric acid and 60% sulfuric acid are incapable of producing isomerization of α-ionone into β-ionone, even at temperatures up to +40°* (Expts. No. 9 and 10).

The data we obtained demonstrate unequivocally that the first process in the cyclization of pseudoionone is the formation of α-ionone, which is capable of a certain degree of isomerization into β-ionone, depending on the reaction conditions. Thus, the reactions whereby these isomers are formed are not parallel, as was previously supposed, but are successive reactions and the specificity of the cyclizing agent reduces to the extent of its isomerizing action.

The method we developed for the cyclization of pseudoionone is a convenient preparative method for obtaining β-ionone and especially α-ionone and may also be of value in the preparation of α-irone.

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THE OXIDATION OF n-BUTANE IN ACETIC ACID SOLUTION WITH AIR UNDER PRESSURE

M. S. Furman, A. D. Shestakova, I. L. Arest-Yakubovich and N. A. Lyubitsyna

State Scientific Research and Planning Institute of the Nitrogen Industry

(Presented by Academician S. I. Vol'fkovich, October 8, 1958)

A series of investigations [1-3] have been devoted to the gas-phase oxidation of butane. A characteristic of this reaction is the formation of a complex range of oxygen-containing compounds (methanol, ethanol, formaldehyde, acetaldehyde, the lower carboxylic acids, acetone and the products of their interaction). This wide range of oxygen-containing compounds arises from the fact that the gas phase oxidation of butane is accomplished at relatively high temperatures (350-400°).

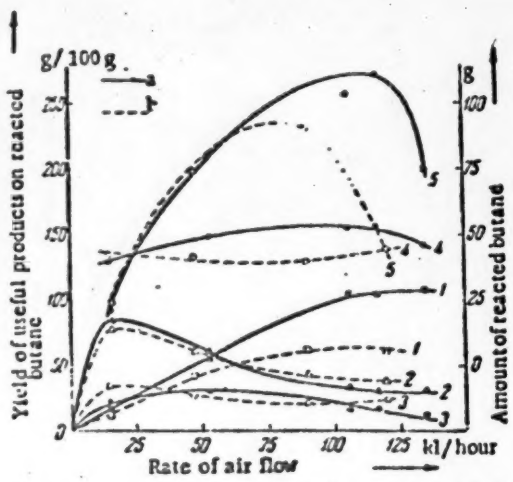

Fig. 1. The effect of rate of air flow on the oxidation of n-butane in a solvent at different temperatures. Pressure, 60 atm.; duration of experiment, 6 hours; amount of catalyst (cobalt stearate), 0.018% of the solvent weight.
1) Acetic acid; 2) ethyl acetate; 3) methyl ethyl ketone; 4) total of useful products; 5) amount of butane reacted; a—165°, b—150°.

In recent years, communications have appeared in the literature [4-8], from which it follows that the oxidation of hydrocarbons may be accomplished under considerably more selective and "mild" conditions in the liquid phase under pressure.

There is particularly great interest in the liquid-phase oxidation of n-butane since, according to existing data, valuable organic products may be obtained from it (acetic acid, ethyl acetate and methyl ethyl ketone).

As follows from the short communications published, the liquid-phase oxidation of butane may be accomplished either at temperatures below the critical temperature of butane (T_k = 152°) [4, 5] or at temperatures above the critical point with the use of a solvent [6-8].

The second method seemed most promising, as the use of a solvent makes it possible to avoid the narrow temperature range dictated by the critical temperature and to vary the oxidation rate widely.

As solvent one may use an organic liquid, which is inert to oxidation under the conditions of the process and which dissolves butane.

We chose acetic acid, which is an oxidation product of butane.

In addition, it is known that the rate of oxidation of hydrocarbons in the phase may be increased by catalysts – salts of variable valence metals and organic acids.

Experiments on the liquid-phase oxidation of n-butane in a solvent were performed in a type of autoclave made of stainless steel with a removable titanium vessel, working with pressure on both sides, making it possible to avoid completely corrosion and the catalytic action of metal acetates formed by corrosion of the walls of the reaction apparatus. The oxidation was achieved with air. Before the reaction, 170 g of n-butane, 170 g of glacial acetic acid and the required amount of catalyst, when the reaction was performed catalytically, were placed in the reactor. During the experiment, the amount of n-butane in the reactor was kept constant by the addition of an amount of butane equivalent to that which reacted and was carried away with the gas.

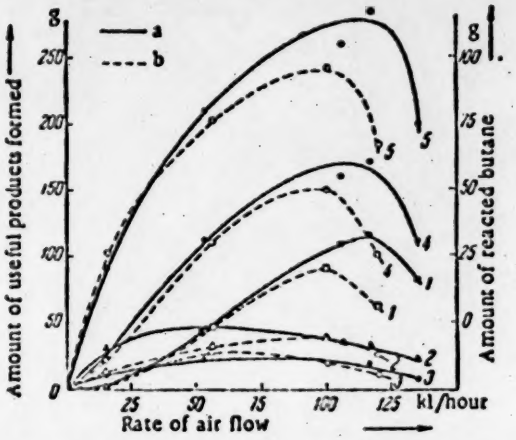

Fig. 2. The effect of the rate of air flow on the catalytic and noncatalytic oxidation of n-butane in a solvent. Pressure, 60 atm.; temperature 165°; duration of experiment, 6 hours.
1) Acetic acid; 2) ethyl acetate, 3) methyl ethyl ketone; 4) total of useful products; 5) amount of butane reacted; a – with catalyst (cobalt stearate, 0.018% of solvent weight), b – without catalyst.

The results of investigating the oxidation of n-butane at temperatures below and above the critical point are shown in Fig. 1. The oxidation was accomplished in acetic acid solution in the presence of catalyst (cobalt stearate) at a pressure of 60 atm with an experiment duration of 6 hours at different air flow rate.

The advantage of carrying out the oxidation of n-butane temperatures above the critical point is obvious from Fig. 1, which shows the increase in the conversion of n-butane with the temperature increase and the rise in the yield of the main useful product – acetic acid.

Fig. 2 shows data on the effect of a catalyst(cobalt stearate) on the oxidation of n-butane at a pressure of 60 atm, a temperature of 165°, and experiment duration of 6 hours and various air flow rates. From the graph it follows that the use of a catalyst increases the conversion of butane, raises the yield of useful products and directs the process toward the predominant formation of acetic acid.

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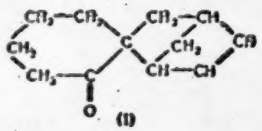
SYNTHESIS OF 6,9-ENDOMETHYLENESPIRO-(4,5)-DECANE

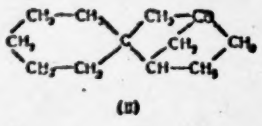
N. V. Elagina, T. V. Stabnikova and Academician B. A. Kazanskii

M. V. Lomonosov Moscow State University

Previously we showed [1] that the diene condensation of 2-methylenecyclohexanone-1 with cyclopentadiene gave an unsaturated spiroketone – 1,4-endomethylenespiro-(5,5)-undecen-2-one-7 (I),



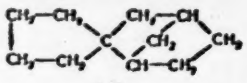
(I)



(II)

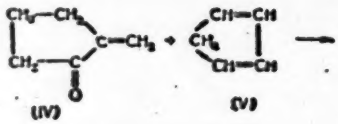
which was converted into a tricyclic spirohydrocarbon – 1,4-endomethylenespiro-(5,5)-undecane (II).

In the present work we used the diene condensation of cyclic α-methyleneketones with cyclopentadiene for the synthesis of yet another representative of the spirohydrocarbons with an endomethylene bridge in the molecule, namely 6,9-endomethylenespiro-(4,5)-decane (III).

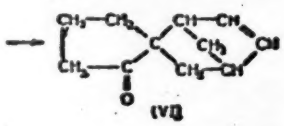


(III)

The reaction of 2-methylenecyclopentanone (IV) with cyclopentadiene (V) gave an unsaturated, tricyclic spiroketone – 6,9-endomethylenespiro-(4,5)-decen-7-one-1 (VI).

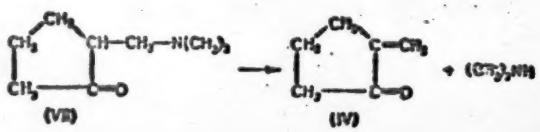


(IV) (V)



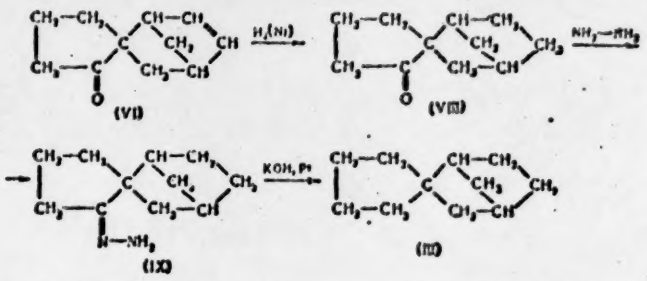
(VI)

Due to its tendency to polymerize, 2-methylenecyclopentanone-1 (IV) was introduced into the reaction as the Mannich base – 2-(N-dimethylaminomethyl)-cyclopentanone-1 (VII) – which decomposed to 2-methylenecyclopentanone-1 and the secondary amine during the reaction.



(VII) (IV)

Catalytic hydrogenation of the ketone (VI) in the presence of Raney nickel in the cold yielded 6,9-endomethylenespiro-(4,5)-decanone-1 (VIII), which was converted to the hydrazone (IX) by treatment with hydrazine hydrate. The latter was decomposed catalytically by N. M. Kizhner's method.



The 6,9-endomethylenespiro-(4,5)-decane was a colorless, mobile liquid with a terpene-like smell and had the following constants: b.p. 83°/12 mm; $n^{20}D$ 1.4899; d^{20}_4 0.9340; MR_D found 46.50, calculated for $C_{11}H_{18}$ 46.40.

EXPERIMENTAL

2-(N-Dimethylaminomethyl)-cyclopentanone-1. Into a 1 liter, three-necked, round-bottomed flask, fitted with a stirrer with a seal, a reflux condenser, a dropping funnel and a gas inlet tube, was placed 168.2 g (2 moles) of cyclopentanone, 81.5 g (1 mole) of dimethylamine hydrochloride and 100 g of 30% formalin solution (d = 1.092), containing 30 g of formaldehyde (1 mole). The reaction was carried out in an atmosphere of nitrogen. The reaction mixture was heated gently. After 15 minutes a reaction began, which was accompanied by boiling of the mixture and at the end of this, the mixture was boiled for a further 10 minutes. 160 ml of water was added to the cooled reaction mixture and the unreacted cyclopentanone was extracted with ether.

133 g of a 30% aqueous solution of sodium hydroxide was added from a dropping funnel with stirring to an aqueous solution of the hydrochloride of 2-(N-dimethylaminomethyl)-cyclopentanone-1 cooled to −5°. The free base separated on the surface of the reaction mixture as an oily layer.

The reaction mixture was extracted with ether and the ether solution dried over anhydrous magnesium sulfate. The ether was removed and the residue vacuum distilled in a stream of nitrogen. A second distillation yielded 56.2 g of 2-(N-dimethylaminomethyl)-cyclopentanone-1 (yield 39.8% of theoretical) with the following constants: b.p. 84°/12 mm; $n^{20}D$ 1.4598; d^{20}_4 0.9449; MR_D found 40.91; calculated for $C_8H_{15}ON$ 40.55.

Found %: C 68.44; 68.34; H 10.58; 10.72; N 9.93; 10 $C_8H_{15}ON$. Calculated %: C 68.05; H 10.71; N 9.92

The colorless, quite mobile liquid had a sharp, amine-like smell.
Literature data [2]: b.p. 88-90°/15 mm.

6,9-Endomethylenespiro-(4,5)-decen-7-one-1. The experiment was performed in a steel autoclave with an electric heater. The temperature was measured with a chromel-alumel thermocouple.

Into a 150 ml glass vessel was placed 42.4 g (0.3 mole) of freshly distilled 2-(N-dimethylaminomethyl)-cyclopentanone-1, 29.7 g (0.45 mole) of cyclopentadiene and 1 g of hydroquinone. The vessel was placed in the reactor of the autoclave, which was heated for 4 hours at 120°. After being cooled, the reaction mixture was dissolved in 200 ml of ether. The ether solution was washed with water, 5% hydrochloric acid, 5% soda solution and again with water and dried over anhydrous magnesium sulfate. The ether was removed and the residue fractionated in vacuum. We obtained 24.1 g of 6,9-endomethylenespiro-(4,5)-decen-7-one-1 (yield 49.5% of theoretical) with the following constants: b.p. 74-74.5°/12 mm; $n^{20}D$ 1.5120; d^{20}_4 1.0584; MR_D found 45.99; calculated for $C_{11}H_{14}OF$ 45.94.

Found %: C 81.28; 81.29; H 8.73; 8.77 $C_{11}H_{14}O$. Found %: C 81.44; H 8.70

The colorless, mobile liquid had a menthol-like smell.

After two recrystallizations from ethyl alcohol, the semicarbazone of 6,9-endomethylenespiro-(4,5)-decen-7-one-1 had m.p. 200.5-201° (with decomp.).

Found %: C 64.97; 65.82; H 7.84; 7.88; N 19.34; 19.37 $C_{12}H_{17}ON_3$. Calculated %: C 65.72; H 7.81 N 19.17

6,9-Endomethylenespiro-(4,5)-decanone-1. Into a hydrogenation vessel of 250 ml capacity was placed 23.5 g (0.145 mole) of 6,9-endomethylenespiro-(4,5)-decen-7-one-1, 1.2 g of Raney nickel and 150 ml of ethyl alcohol. Over a period of 2.5 hours, 3226 ml (0°, 760 mm) of hydrogen was absorbed and after this the hydrogenation rate fell sharply and the experiment was stopped. The alcohol was removed and the ketone dried over anhydrous magnesium sulfate and vacuum distilled. We obtained 22.53 g of 6,9-endomethylenespiro-(4,5)-decanone-1 (yield 94.7% of theoretical) with the following constants: b.p. 86°/2 mm; $n^{20}D$ 1.5020; d^{20}_4 1.0402; MR_D found 46.60, calculated for $C_{11}H_{16}O$ 46.41.

Found %: C 80.71; 80.67; H 9.73; 9.82 $C_{11}H_{16}O$. Calculated %: C 80.44; H 9.82

The colorless liquid had a weak menthol-like smell.

After the two recrystallizations from ethyl alcohol, the semicarbazone of 6,9-endomethylenespiro-(4,5)-decanone-1 had m.p. 206.5-207.5°.

Found %: C 65.40; 65.23; H 8.69; 8.56; N 18.92; 19.06 $C_{12}H_{19}ON_3$. Calculated %: C 65.11; H 8.65; N 18.98

After two recrystallizations from ethyl alcohol, the oxime of 6,9-endomethylenespiro-(4,5)-decanone-1 had m.p. 95-95.5°.

Found %: C 73.35; 73.47; H 9.44; 9.45; N 8.06; 8.14 $C_{11}H_{17}ON$. Calculated %: C 73.70; H 9.56; N 7.81

6,9-Endomethylenespiro-(4,5)-decane. Into a 500 ml round-bottomed flask was placed 82.1 g (0.5 mole) of 6,9-endomethylene-(4,5)-decanone-1, 55.6 g (1 mole) of 90% hydrazine hydrate and 100 ml of ethyl alcohol. The flask was connected to a reflux condenser and heated for 6 hours on a glycerol bath, whose temperature was kept at 115°. Then the alcohol and the unreacted hydrazine hydrate were distilled off from the reaction mixture. Solid potassium hydroxide was added to the residue. The hydrazone, which separated on the surface of the reaction mixture as an oily layer, was separated and dried over fused potassium hydroxide. We obtained 93.6 g of the hydrazone of 6,9-endomethylenespiro-(4,5)-decanone-1 as a thick, light yellow oil. The hydrazone was decomposed catalytically without preliminary distillation.

Into a 150 ml Wurtz flask, fitted with a thermometer and connected to a distillation condenser, was placed the hydrazone 6,9-endomethylenespiro-(4,5)-decanone-1, 2 g of freshly fused potassium hydroxide and 0.1 g of platinized charcoal. The mixture was heated on a metal bath, whose temperature was gradually raised. At 170°, the hydrozone began to decompose vigorously. The hydrocarbon distilled off at a bath temperature of 230-240° with the emergent vapor at 210-220°. The distillate was dried over fused potassium hydroxide and distilled over a new portion of catalyst. The hydrocarbon obtained was washed with 50% acetic acid, water, 3% potassium hydroxide solution and again with water, dried over fused potash and vacuum distilled over metallic sodium. We obtained 52.5 g of 6,9-endomethylenespiro-(4,5)-decane (yield 70% of theoretical) with b.p. 78°/10 mm.

The hydrocarbon obtained was vacuum distilled on a fractionating column with a metal packing with an efficiency of 40 theoretical plates. We obtained a total of 88 g of 6,9-endomethylenespiro-(4,5)-decane with the following constants: b. p. 76°/8 mm, 83°/12 mm; $n^{20}D$ 1.4899; d^{20}_4 0.9340; MR_D found 46.50; calculated for $C_{11}H_{18}$ 46.40

Found %: C 87.78; 87.73; H 12.24; 12.10; $C_{11}H_{18}$. Calculated %: C 87.92; H 12.08

The quite mobile, colorless liquid had a characteristic terpene-like smell.

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THE PHASE COMPOSITION OF ALLOYS OF THE SYSTEM COBALT – BORON

P. T. Kolomytsev

N. E. Zhukovskii Air Force Engineering Academy

(Presented by Academician L. P. Bardin, November 6, 1958)

The alloys of the system cobalt – boron have been studied by a series of investigators, who identified several compounds of cobalt with boron.

The presence of the compounds Co_2B and CoB_2, in addition to the compound CoB, known at that time, was reported in the paper by Binet du Jassonneux [1].

TABLE 1

x-Ray Data for Co_2B (CoK_α radiation)

Expt. no.	I	$\sin^2\theta$	d, kX	Expt. no.	I	$\sin^2\theta$	d, kX
1	weak	0,1355	2,42	17	very weak	0,5268	1,23$_0$
2	strong	0,1432	2,36	18	medium	0,5644	1,18$_8$
3	medium	0,1581	2,24	19	weak	0,5730	1,17$_9$
4	strong	0,1766	2,12	20	strong	0,5928	1,15$_9$
5	strong	0,1915	2,04	21	medium	0,6142	1,13$_9$
6	strong	0,1942	2,02$_6$	22	strong	0,6336	1,12$_2$
7	strong	0,2052	1,97$_6$	23	weak	0,6492	1,108
8	strong	0,2123	1,93$_3$	24	weak	0,6578	1,100
9	strong	0,2328	1,85$_9$	25	very weak	0,6910	1,073
10	medium	0,2668	1,72$_4$	26	weak	0,7595	1,024
11	weak	0,2800	1,68$_7$	27	very weak	0,7981	0,999
12	medium	0,3056	1,61$_3$	28	strong	0,8469	0,970
13	very weak	0,3213	1,57$_4$	29	very weak	0,8843	0,949
14	medium	0,4741	1,29$_7$	30	medium	0,9033	0,934
15	very weak	0,5026	1,25$_9$	31	very weak	0,9343	0,919
16	medium	0,5049	1,25$_9$	32	weak	0,9596	0,911

Bjürström [2] carried out an x-ray analysis of the alloys of the cobalt – boron system. He examined the crystalline structure of the compounds Co_2B and CoB and showed that these compounds were isomorphous with the corresponding borides of iron, Fe_2B and FeB. By analyzing alloys with larger boron contents, Bjürström demonstrated the possibility of yet another phase existing in the system Co – B. Köster and Müllinger [3] considered that the first intermetallide phase in the Co – B system on the cobalt side was the compound Co_2B with a melting point of 1265°. From data on thermal and magnetic analysis, the authors of the work [3] constructed a phase diagram for the Co–B system up to 8.41% B.

Academician N. P. Chizhevskii and B. A. Shmelev examined the alloys of the cobalt – boron system in detail [4]. The authors carried out thermal analysis, metallographic and x-ray examinations and hardness and specific gravity determinations on alloys containing from 0.76–9.20% of boron and constructed a phase diagram, similar to the phase diagram of the Fe – B system.

To examine the alloys of cobalt with boron, we prepared 20 samples, which contained 4% and more of boron.

Fig. 1. Microstructure of alloys in the cobalt – boron system: a) 7% B; b) 8.2% B. 500x

Fig. 2. Microstructure of alloys of the cobalt – boron system: a) 15.3% B; b) 15.7% B. 500x

For the preparation we used charges of powdered cobalt, containing 99.43% cobalt, 0.21% nickel, 0.1% iron, 0.01% copper, 0.09% oxygen and 0.03% silicon, and amorphous boron, obtained by thermal dissociation of diborane, fired in vacuum and containing not less than 99.5% boron. The charges were carefully mixed and compressed.

Samples weighing 10 g, melted in an atmosphere of pure argon, were homogenized at 1000° for 50 hours.

The alloys were x-rayed, using the powder methodand analyzed microscopically to measure the microhardness on a PMT-3 apparatus under a load of 50 g. Marks from microhardness measurements can be seen on the microphotographs presented later.

As a result of investigations in the cobalt – boron system, 4 compounds were identified – Co_3B, Co_2B, CoB and a η-phase, apparently the diboride CoB_2.

With a boron content of from 4 to 5.76%, the structure of the alloys consisted of an eutectic of $\alpha + Co_3B$ and excess crystals of the compound Co_3B. An increase in the boron content above 5.8% leads to the appearance in the structure of the alloys of the compound Co_2B, which was identified by both metallographic and x-ray methods. Fig. 1 shows microphotographs of alloys containing 7 and 8.2% of boron, in which the Co_3B crystals are dark. The structure of the alloy with 7% of boron consists predominantly of grains of Co_3B and light grains of Co_2B. Crystals of Co_2B form less of the structure of the alloy with 8.2% boron.

An increase in the boron content from 8.4 to 15.5% leads to a decrease in the Co_2B and an increase in the CoB content of the alloy structure. No stable intermediate phases were observed between the compounds Co_2B and CoB.

With the boron content of 15.6% and more in the alloys, a new constituent appears in the structure and this we call the η-phase.

TABLE 2

x-Ray Data for CoB (CoK_α radiation)

Expt. no.	I	$\sin^2\theta$	d, kX	Expt. no.	I	$\sin^2\theta$	d, kX
1	very weak	0,0580	3,70	13	weak	0,5165	$1,24_8$
2	very weak	0,0789	3,17	14	strong	0,5531	$1,20_9$
3	weak	0,1153	2,63	15	strong	0,5809	$1,17_3$
4	medium	0,1371	2,41	16	medium	0,6595	1,099
5	very strong	0,1691	2,17	17	weak	0,7239	1,049
6	strong	0,2031	1,98	18	very weak	0,7796	1,010
7	strong	0,2341	$1,84_6$	19	weak	0,8160	0,988
8	medium	0,2535	$1,77_2$	20	very strong	0,8625	0,961
9	medium	0,3132	$1,59_3$	21	very weak	0,8791	0,952
10	medium	0,3208	$1,57_6$	22	weak	0,9251	0,928
11	weak	0,3469	$1,51_6$	23	weak	0,9455	0,918
12	very weak	0,4657	$1,30_3$				

Fig. 2. shows the microstructure of alloys containing 15.3 and 15.7% of boron. The main component of the structure of these alloys is the compound CoB. In the alloy with 15.3% boron, the second constituent is the boride Co_2B and in the alloy with 15.7% B, small inclusions of the η-phase, on which can be seen the impression of a diamond-shaped pyramid. The microstructure of the alloy with the greatest amount of boron which we were able to introduce (Fig. 3), consists predominantly of the η-phase and a small amount of the boride CoB.

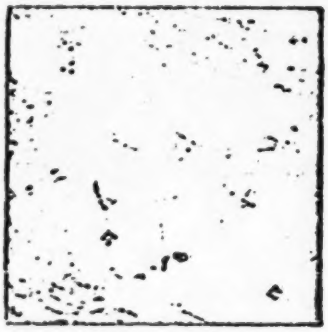

Fig. 3. Microphotograph of an alloy with the structure of the η-phase + CoB. 500 x

Comparison of the dimensions of the marks of the diamond-shaped pyramid on the microphotographs presented shows that the η-phase is distinguished by great hardness.

Measurements of the microhardness showed that the borides Co_3B, Co_2B and CoB possess the same hardness, equal to 1145 kg/mm², while the microhardness of the η-phase is 2575 kg/mm²

The compound Co_3B has a grey color and a melting point of 1180°. The melting point was determined by constructing the cooling curve. For this purpose a 30 g sample was melted and cooled under vacuum at 10^{-2}-10^{-3} mm.

The x-ray data for Co_3B, obtained with CoK_α radiation with an iron foil filter, are presented in Table 1 and x-rays of compounds Co_3B, Co_2B and CoB in Fig. 4.

The data presented indicate that the crystal lattice of Co_3B is isomorphous with Ni_3B, on which we presented the x-ray data in the paper [5] followed by N. I. Blok and M. N. Kozlova et al. in paper [6].

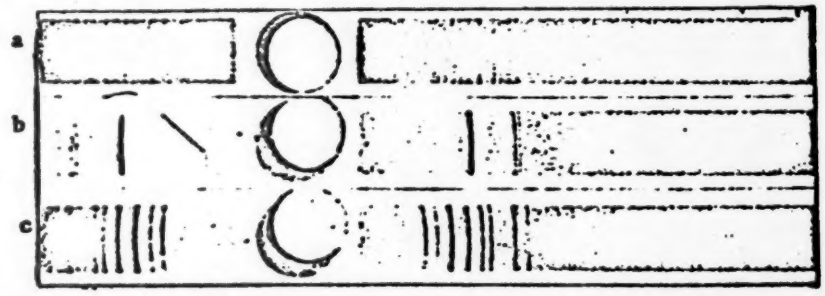

Fig. 4. x-Rays of the boride: a) Co_3B; b) Co_2B; c) CoB.

The x-ray data for Co_2B, obtained on our samples, confirmed the statement of Bjūrström [2] et al., that the lattice of Co_2B was isomorphous with the lattices of Fe_2B and Ni_2B.

The disposition of the lines in the x-radiogram of the boride CoB (Fig. 4) differs considerably from the x-ray of the boride FeB, presented by Wever and Müller [7] and x-ray data for compound CoB, presented in Table 2, differs from the results obtained in work [2] and do not indicate that the lattices of the compounds CoB and FeB are isomorphous.

As a result of an investigation of the cobalt – boron system, the compound Co_2B was detected for the first time and its lattice found to be isomorphous with Ni_2B and x-ray data for compound CoB was determined more accurately. It was established that in the cobalt-boron system, the compounds Co_2B, Co_2B, and CoB have almost identical microhardness equal to 1145 kg/mm^2 and the microhardness is increased by a factor of more than two to 2575 kg/mm^2 with the formation of the η-phase, which is richer in boron.

The authors are very grateful to Professor I. I. Kornilov for his interest in the work and to S. A. Strekopytov for help with the experiments.

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VINYL ESTERS OF PHOSPHOROUS ACID

Academician A. N. Nesmeyanov, I. F. Lutsenko,
Z. S. Kraits and A. P. Bokovoi

M. V. Lomonosov Moscow State University

In recent years a considerable number of papers have appeared on unsaturated esters of acids of phosphorus and this is connected with the fact that they have certain peculiarities [1].

The few known representatives of full unsaturated esters of phosphorous acid are compounds of the allyl series and were prepared by A. E. Arbuzov and V. M. Zoroastrova and also by G. Kamai and N. A. Chadaeva [2]. No example of a vinyl ester of phosphorous acid is known since the general methods of synthesizing esters of phosphorous acid, including allyl ones, are not applicable.

At the same time, vinyl esters of phosphorous acid in particular would be expected to have a series of peculiarities in their chemical behavior and above all in the Arbuzov rearrangement. Thus, though the allyl ester of phosphorous acid rearranges only slightly more slowly than trimethyl phosphite, trivinyl phosphite should be similar to the phenyl ester of phsophorous acid in this respect.

In order to study the conditions and also the direction of the isomerization of vinyl esters of phosphorous acid, we prepared both compounds of the type $(RO)_2POCH=CH_2$ and $ROP(OCH=CH_2)_2$ and also trivinyl phosphite itself $P(OCH=CH_2)_3$.

For the synthesis of vinyl esters of phosphorous acid, we used the reaction discovered by A. N. Nesmeyanov, I. F. Lutsenko and Z. M. Tumanova [3], which consists of the acylation of α-monomercurated oxo compounds and proceeds with the transfer of the reaction center.

Preliminary experiments on the reaction of chloromercuriacetaldehyde and diethyl chlorophosphite showed that the reaction proceeded readily, even in the cold, by the equation:

$$ClHgCH_2CHO + ClP(OR)_2 \rightarrow CH_2=CHOP(OR)_2HgCl_2$$

however, the yields of vinyl esters obtained were very low and the substance was difficult to purify. This is undoubtedly connected with the well-known fact that esters of phosphorous acid react with mercuric chloride [4]. To remove this difficulty, we reacted diethyl chlorophosphite with mercuribisacetaldehyde in isopentane and did not carry the reaction on to the formation of mercuric chloride, but only to chloromercuriacetaldehyde.

$$Hg(CH_2CHO)_2 + ClP(OR)_2 \rightarrow CH_2=CHOP(OR)_2 + ClHgCH_2CHO$$

In this case, the dialkyl vinyl phosphites were obtained in a yield of about 40%. In the preparation of alkyl divinyl phosphite from Menshutkin's acid chloride and mercuribisacetaldehyde, strong polymerization was observed, even at the very beginning of the reaction. The addition of an equivalent amount of base made it possible to depress polymerization and to obtain the alkyl divinyl esters in 50-60% yield. The reaction of dialkyl chlorophosphite with mercuribisacetaldehyde in the presence of base gave higher yields of dialkyl vinyl phosphites (60-70%). Triethylamine was the base used in all cases except with methyl derivatives, when diethylamine was used. Similarly trivinyl phosphite was obtained from phosphorous trichloride and mercuribisacetaldehyde.

TABLE 1

Vinyl Esters of Acids of Phosphorus

	Yield, %	B.p.	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % P	Calculated, % C	Calculated, % H	Calculated, % P
$(CH_2O)_2POR$*	46	55—56°/80 mm.	1,4255	1,0406	33,46	33,27	35,63	6,60	22,37	35,30	6,66	22,76
$(C_2H_3O)_2POR$	67	58—59°/28 mm	1,4258	0,9787	42,91	42,51	43,30	8,03	18,26	43,90	7,98	18,87
$(C_3H_5O)_2POR$	62	53—54°/3 mm	1,4322	0,9518	52,39	51,74	49,67	8,87	16,37	49,99	8,91	16,12
$(C_4H_7O)_2POR$	70	85—86°/4 mm.	1,4360	0,9381	61,45	60,98	54,52	9,35	13,98	54,53	9,61	14,06
$(C_6H_5O)_2POR$	80	143—144°/3 mm	1,5575	1,1567	72,25	72,26	64,62	5,11	12,19	64,60	5,03	11,90
$CH_3OP(OR)_2$	56	60—61°/60 mm.	1,4390	1,0368	37,37	37,42	40,72	6,03	20,47	40,54	6,12	20,92
$C_2H_5OP(OR)_2$	60	57—58°/30 mm	1,4380	1,0015	42,47	42,03	44,31	6,65	19,49	44,50	6,84	19,12
$C_3H_7OP(OR)_2$	62	56—57°/11mm	1,4392	0,9908	46,78	46,66	47,67	7,34	17,59	47,73	7,44	17,59
$C_4H_9OP(OR)_2$	60	63°/7 mm	1,4412	0,9873	51,18	51,28	50,32	7,85	16,58	50,52	7,95	16,29
$C_6H_5OP(OR)_2$	55	108—109°/10 mm	1,5151	1,1037	56,91	57,46	56,91	5,13	14,92	57,15	5,28	14,74
$P(OR)_3$	46	51—52°/30 mm	1,4185	1,0262	41,57	41,81	45,05	5,61	19,28	45,01	5,67	19,35
$(C_2H_3O)_2P(S)OR$	64	82°/7,5 mm	1,4562	1,0904	48,93	48,91	36,90	6,69	16,15	36,73	6,68	15,79
$(C_3H_5O)_2P(S)OR$	67	97°/6 mm	1,4581	1,0505	58,21	58,15	43,02	7,52	13,90	42,84	7,64	13,82
$(C_4H_7O)_2P(S)OR$	50	126—127°/8 mm	1,4575	1,0195	67,40	67,38	47,92	8,47	12,54	47,60	8,39	12,28
$(C_6H_5O)_2P(S)OR$	62	163—164°/2 mm	1,5655	1,2164	78,64	78,33	57,55	4,50	10,43	57,52	4,48	10,60
$C_2H_5OP(S)(OR)_2$	65	72—73°/7 mm	1,4634	1,1017	48,58	48,44	37,41	5,58	16,19	37,11	5,71	15,95
$C_3H_7OP(S)(OR)_2$	74	96°/6 mm	1,4654	1,0617	57,91	57,68	43,42	6,57	14,08	43,23	6,80	13,94
$C_6H_5OP(S)(OR)_2$		134—135°/10 mm	1,5208	1,1719	63,31	63,52	49,55	4,58	13,34	49,58	4,58	12,79

*Here and later R = CH=CH$_2$.

To obtain the vinyl esters of phosphorous acid in the yields given it was best to introduce not more than 0.1 mole of mercury organic compound and amine into the reaction flask at one time. After the addition of an equivalent amount of chlorophosphite, the next portion of mercuribisacetaldehyde and amine was introduced.

The vinyl phosphites were readily hydrolyzed by water with considerable evolution of heat. The addition of Schiff's reagent immediately gave the characteristic color. Trivinyl phosphite was rapidly hydrolyzed by even traces of moisture to form a white gel-like mass immediately, which evolved heat strongly after 1-2 min and darkened due to tar formation by the acetalydehyde liberated. The constants, yields and analytical data of the esters obtained are given in Table 1. Vinyl esters of phosphorous acid added sulfur, when heated on a boiling water bath for 6-8 hours. The constants and yields of the thiophosphates are given in Table 1.

The oxidation of vinyl esters of phosphorous acid under various conditions so as to prepare vinyl esters of phosphoric acid was unsuccessful due to ready polymerization.

At the present time we are studying the isomerization reactions of the vinyl phosphites obtained and these proceed with greater difficulty than those of trialkyl phosphites.

EXPERIMENTAL

Preparation of diethyl vinyl phosphite. 0.1 mole of mercuribisacetaldehyde and 0.1 mole of triethylamine were added to 250 ml of isopentane; then 0.1 mole of diethyl chlorophosphite in 50 ml of isopentane was added over a period of an hour with vigorous stirring. After this, 0.1 mole of mercuribisacetaldehyde and 0.1 mole of triethylamine were again introduced, 0.1 mole of diethyl chlorophosphite added and the reaction mixture was stirred for a further hour. The isopentane was poured off from the precipitate and the residue was washed with isopentane (2x 50 ml). The solvent was removed and the residue distilled in a stream of nitrogen. Two distillations yielded 20.5 g (63% of theoretical) of diethylvinyl phosphite.

Preparation of ethyl divinyl phosphite. 0.1 mole of mercuribisacetaldehyde and 0.1 mole of triethylamine was introduced into 250 ml of isopentane and a solution of 0.05 mole of ethyl dichlorophosphite in 25 ml of isopentane was added over a period of an hour with vigorous stirring. Then the same amounts of organomercury compound and base were interduced and the next 0.05 mole of ethyl dichlorophosphite added. Over a period of 4 hours, 120 g (0.42 mole) of mercuribisacetaldehyde, 40.4 g (0.4 mole) of triethylamine and 29.4 g (0.2 mole) of ethyl dichlorophosphite were introduced into the reaction, then the reaction mixture was stirred for a further 1 hour, the solvent poured off from the precipitate and the residue washed with isopentane (2 x 50 ml). The isopentane was distilled from the combined solutions and the residue distilled in a stream of nitrogen. Two distillations yielded 19.8 g (60% of theoretical) of ethyl divinyl phosphite.

Preparation of trivinyl phosphite. Over a period of 3 hours, 135 g (0.48 mole) of mercuribisacetaldehyde, 45.5 g (0.45 mole) of triethylamine and 20.5 g (0.15 mole) of phosphorus trichloride were introduced into 250 ml of isopentane in 4 equal portions, then the reaction mixture was stirred for a further 1 hour, the solvent poured from the precipitate and the residue washed with isopentane (2x 50 ml). The isopentane was removed and the residue distilled in a stream of nitrogen. Two distillations yielded 11 g (46% of theoretical) of trivinyl phosphite.

Addition of sulfur to diethyl vinyl phosphite. 4.8 g (0.03 mole) of diethyl vinyl phosphite and 1 g of sulfur were heated under reflux on a boiling water bath for 8 hours.

The excess sulfur was sucked off and washed with 2 ml of isopentane and the filtrate distilled in vacuum. We obtained 4.5 g (79% of theoretical) of diethyl vinyl thiphosphate. Phenyl divinyl phosphite and diphenyl vinyl phosphite added sulfur, when the mixture was heated at 130-150° for 8 hours.

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THE POLYMERIZATION OF α-BUTENE WITH A COMPLEX ORGANOMETALLIC CATALYST $Al(C_2H_5)_3 + TiCl_4$

Academician A. V. Topchiev, B. A. Krentsel',
N. A. Pokatilo and E. L. Erasova

Aspects of stereospecific polymerization of α-olefins with complex organometallic catalysts have attracted the growing attention of many investigators in recent years. This is explained both by the theoretical interest of polymerizations with the production of stereoregular polymers and by the technically valuable properties of the products formed. After J. Natta's discovery of the synthesis of stereoregular polypropylene, many communications have appeared in the press on the investigation of the mechanism of stereospecific polymerization of α-olefins and the properties of the polymers obtained. This work has been collected into published review articles by Soviet and foreign authors [1-4].

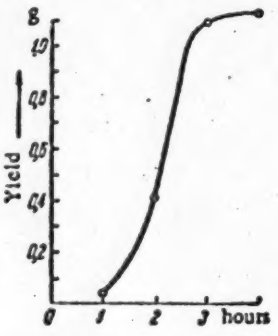

Fig. 1. Dependence of polybutylene yield on reaction time.

There is little data contained in the literature on the preparation of high-molecular polymers based on α-butene. Apart from isolated references in the works of Natta et al. [5-8] on the properties and structure of polybutene, there are no communications on this problem. In connection with this, it seemed interesting to us to investigate some aspects of the polymerization of α-butene with the catalyst $Al(C_2H_5)_3 + TiCl_4$.

EXPERIMENTAL

The starting butene was prepared by dehydration of n-butanol over active aluminum oxide at a temperature of 380-400°. According to vapor phase chromatography (support – firebrick, reagent – isoamyl phthalate), the gas obtained contained butene-1, 67.88%, butene-2-cis, 14.54% and butene-2-trans, 17.58%. The triethylaluminum was synthesized by a direct method from ethylene, aluminum and hydrogen.* The triethylaluminium was used in a solution of purified benzine and according to analysis, it contained 54.38% of active $Al(C_2H_5)_3$, 7.3% of ethoxy compound, 2.0% of

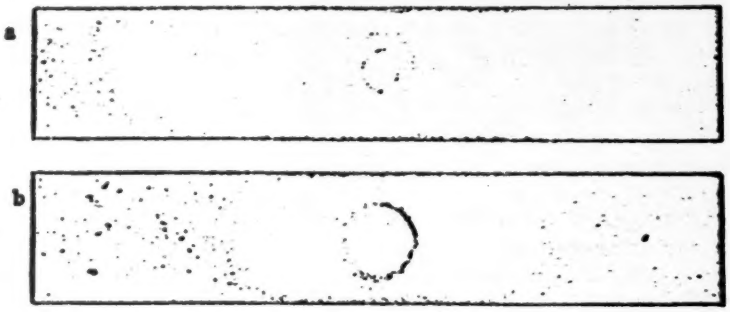

Fig. 2. x-Ray of crystalline (a) and amorphous (b) polybutylene.

* The triethylaluminum was synthesized by A. F. Popov, whom we take this opportunity to thank.

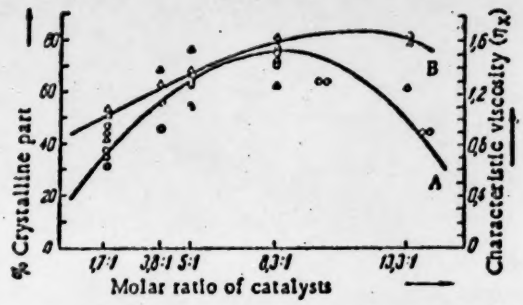

Fig. 3. Dependence of the characteristic viscosity of polybutylene (A) and content of crystalline part in polybutylene (B) on the molar ratio of the catalysts ($C_2H_5)_3Al$: $TiCl_4$

diethylaluminum hydride and 36.32% of solvent. The $TiCl_4$ used was commerical, analytical grade.

The reaction was performed in dry n-heptane (distilled several times over metallic sodium and stored over metallic sodium). The whole reaction system was first carefully flushed with dry nitrogen, freed from oxygen, and the experiment performed under the conditions accepted for work with organometallic compounds.

In all the experiments, the total amount of catalyst in solvent used was 5% and the reaction time 4 hours. As the graph in Fig. 1 shows, a further increase in the reaction time was not advantageous.

At the end of the reaction, the residual catalyst was decomposed with isopropyl alcohol. The solid polymer obtained was washed with isopropyl alcohol containing a small amount of hydrochloric acid and then treated successively with pure isopropyl alcohol and not water. The washed polymer was dried to constant weight at 60-70°. The product treated in this way contained up to 0.2% of ash.

The prepared polymer was characterized by the melting point, characteristic viscosity and a hot fractionation with the help of ether and n-heptane [9]. We should note that according to the data of Natta et al. [8] a certain part of poorly crystalline poly-α-butene may be dissolved in boiling n-pentane, after extraction with ether. However, this was not confirmed by our preliminary experiments and therefore, we retained the order of extraction given above. The part of the polymer dissolving in boiling ether was taken as amorphous and that dissolving in heptane as crystalline. This agrees with the data given below on the x-ray structural analysis, performed by V. V. Shchekin and S. A. Gol'din and the authors would like to thank them for this (Fig. 2).

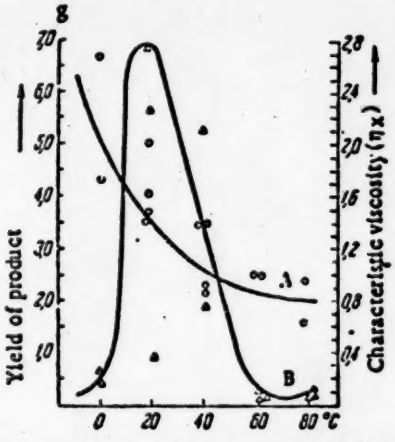

Fig. 4. Dependence of characteristic viscosity of polybutylene (A) and the polybutylene yield (B) on the reaction temperature.

The characteristic viscosity of polybutene was determined by the usual method in decalin solution at 120°. As the graph illustrated in Fig. 3A shows, the ratio between the catalyst components has a significant effect on the characteristic viscosity of the polymer (temperature of experiments, 20°) There is a clearly expressed maximum in the characteristic viscosity, corresponding to a molar ratio of $Al(C_2H_5)_3$: $TiCl_4$ 8.3:1. However, as follows from the graph shown in Fig. 4A and which refers to a series of experiments carried out with the optimal ratio of catalyst components, with an increase in temperature, the characteristic viscosity of the polymer falls sharply and only at temperatures above 50° is the characteristic viscosity and consequently the chain-length of the polybutene macromolecules practically independent of temperature.

In addition, the content of the crystalline part of the polymer also depends on the molar ratio between the catalyst components. This is illustrated by the graph in Fig. 3B, which passes through a maximum, close to the maximum for the curve of the dependence of characteristic viscosity on the molar composition of the catalyst. Thus there is a clear relation between the content of crystalline part in the polymer and its molecular weight,

i. e. an increase in the content of the crystalline part is accompanied by an increase in the molecular weight. The yield of the polymer is affected by the reaction temperature and, as is shown by Fig. 4B, the optimum yield is observed at a reaction temperature between 20 and 30° under the condition of our experiments. The molar composition of the catalyst also has some effect on the polymer yield, but this is not marked.

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